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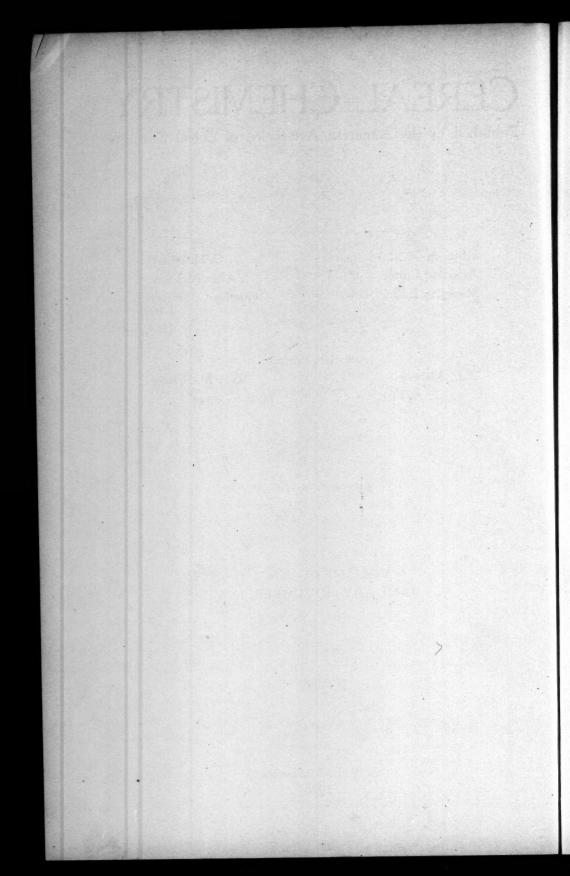
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No. 1

SOME VARIABLE FACTORS OF BREAD PRODUCTION

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(Read at the Convention, June 4, 1925)

Experience in both the experimental bakeshop and the plant has indicated that when trouble occurs in the production of bread, in a majority of cases it is not due to the flour, but to some of the variables of bread production that are not being properly controlled. This is true not only in commercial production of bread, but research workers and laboratories of excellent standing may make splendid physical and chemical measurements, and then fail in the actual production of bread. There is very little concrete information available on this subject.

The variables of bread production are many and only a few can be discussed in this paper. By way of introduction some of the more common variables should be considered. Absorption is one of the most vital factors in the production of bread because it directly influences the volume and quality of the bread as well as the profits of bread manufacture. What is absorption? This we do not know in exact scientific terms, but in the language of the baker it is the quantity of water necessary to give the dough the proper consistency for the production of bread that is his ideal. Graph 1 shows the importance of absorption with reference to volume. In bakes conducted under the same conditions, we obtained an increase in volume of 750 cc. when the absorption was increased from 50% to 65%. Upon further increasing it to 75% there was a decrease in volume of 600 cc.

Table I shows the improvement in the quality of the bread, which in this case reaches its maximum between 60% and 65%. It is a common practice of many bakers and research workers to have too little water in their doughs. There are cases on record of absorptions as low as 51 per cent for bread poduction. It may be that bread can be produced with this absorption, but so far as my knowledge and experience go, a bread flour has never been observed that will give its best results with this low absorption with any speed or type of mixer. These data can be only relative, as mixer speed, salt content, and many other factors influence absorption.

Tracer Michel

TABLE I VARIATIONS CAUSED BY DIFFERENT ABSORPTIONS ON PROPERTIES OF BREAD

Absorption, Per cent.	Volume of loaf cc.	Spring in	Color of crumb	Color of	Flavor	Grain	Texture
50	2550	F*	G—	G	G	G—	G-
55	3100	F+	G	G	G	G	G
60	8275	G	G	G	G	G	G
65	8800	G	G	G	G	G	G
70	8150	G-	G	G	G	G	G
75	2700	F	1	G	G-	G	G

^{*} Key to grading: F=fair, F+=fair plus, G=good, G+=good plus,

The correct panning of dough is exceedingly important. If two loaves are panned from the same dough, No. 1 being placed slightly to the side of the pan and No. 2 in the middle, it will be observed from Table II that this makes the difference between salable and unsalable bread.

TABLE II VARIATIONS FROM METHODS OF PANNING ON PROPERTIES OF BREAD

Loaf	Volume	Spring	Color	Color			
No.	of loaf, cc.	in oven .	of crumb	of crust	Flavor	Grain	Texture
1	2700	F	G	G	G	G—	G-
2	3280	G	G	G	G	G	G

No. 1, in order to fill the pan, had to turn over. The label that was placed on the top of the moulded dough was found almost on the bottom of the baked loaf. The turning caused a tearing of the dough, which allowed the gas to escape and resulted in a loaf of very inferior volume and appearance.

Another factor that might appear very unimportant is that of pan greasing. In Table III the larger loaf was produced in an ungreased pan. The smaller loaf was produced in a heavily greased pan. Both loaves were from the same dough. Pan greasing should be carefully controlled, from both an economical standpoint and one of quality in bread production. It is one point that must be observed by the research worker. To grease pans on each bake, as is often done, certainly makes a very great and absolutely unnecessary error in final results.

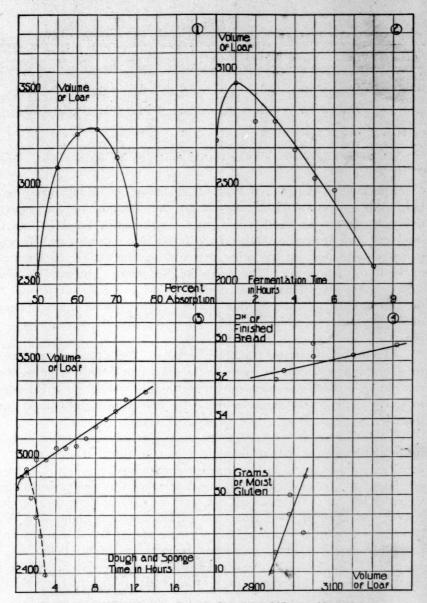
TABLE III EFFECT OF PAN GREASING ON PROPERTIES OF BREAD

Treatment	Volume of loaf, cc.			Color of crust	Flavor	Grain	Texture	
Greased	2900	F+	G	G	G	G	G	
Ungreased	3400	G	G	G	G	G	G	
	9/4/9		*:	, iii		v	•	

30: N TO CONT.

⁻⁼good minus, P=poor, P-=poor minus.

[†] Slightly dull.



Graph 1. Variations in Volume Caused by Different Absorptions

Graph 2. Relation of Fermentation Period and Volume of Bread Produced from Straight
Doughs

Graph 3. Relation of Fermentation Period and Volume of Bread Produced from Sponge Doughs

Graph 4. Effect of Dough Acidity on Volume

TABLE IV
INFLUENCE OF NUMBER AND FREQUENCY OF PUNCHES ON PROPERTIES OF BREAD

Time punched	Volume of loaf, cc.	Spring in oven		Color of crust	Flavor	Grain	Texture	Absorp- tion per cent	tation
Every						1.5			
15 min.	8350	G	G	G	G	G	G	67	8
Every									
80 min.	8870	G	G	G	G	G	G	67	8
At end of									
14 hours	8340	G	G	G	G	G	G	67	8
No punche	8875	G	G	G	G	G	G	67	8

* This fermentation was on a 3-hour straight dough with 2½ per cent yeast. Temperature 80°F.

Punching of doughs has been much discussed. Many firmly believe in the proverbial 65, 25, and 15% of the total time for the respective first and second punches and pan. As shown in Table IV, there was very little difference between the bread that was obtained by not punching, and that, on the other extreme, punched every 15 minutes of the fermentation time. The dough punched every 15 minutes showed slightly more age. This might possibly be due to a removal of one of the end products, carbon dioxide, which together with a slight amount of oxygen from punching, would tend to increase the activity of the yeast.

The period of mixing at a given speed and for a constant time and to a given temperature is exceedingly important. This requires the calculation of the correct amount of ice or cold water to use in order to arrive at the correct temperature of the finished dough in the stated time.

Table V gives an idea of the increase in volume and general quality of the bread through an increase in mixing time. Temperature is equally as important as mixing time or revolutions per minute. These are important factors that are often overlooked. A few months ago a service laboratory was visited that was sending reports to commercial bakers and advising them how best to ferment their flours. In this laboratory the doughs were mixed anywhere from 3 to 7 minutes and they did not come out at a constant temperature. This is far from scientific. The American Association of Cereal Chemists has made a great move forward in attempting to standardize the method of baking.

TABLE V
EFFECT OF MIXING TIME ON PROPERTIES OF BREAD

Time mixed minutes	Volume of loaf, cc.	Spring in oven			Flavor	Grain		Absorption per cent	Fermen- tation hours
8	2800	F+	G—	G	G	G-	G-	66	8
9.5	3400	G	G	G	G	G	G	66	- 3
13	8600	G+	G	G	G	G	G	66	3
17	3550	G+	G	G	G	G+	G+	66	3

Thus far we have discussed only some of the more common variable factors that occur in the handling of the dough. Now let us consider the broader subject, fermentation, which in my opinion is the most important single factor in bread production. Before discussing this subject it is advisable to make a definite classification of bread doughs. This will prevent a great deal of misunderstanding that has occurred in the past. Doughs can be divided into two classes: (1) Straight doughs, that is, doughs in which all the flour and yeast are acting together in the presence of the added electrolytes, namely, salt, for the total time of fermentation, (2) Sponge dough, or batter type, in which only a part of the flour and all or part of the yeast are allowed to act together for a certain percentage of the total time of fermentation without salt. This is known as the sponge time. The rest of the ingredients are added with the salt and then allowed to ferment the remaining time. The latter period is known as the dough time. The results obtained with these two types of doughs are very different and an example of each will be given.

Graph 2 shows the results obtained from the straight dough made from a short patent flour, with $2\frac{1}{2}\%$ yeast, $\frac{1}{2}\%$ Arkady, and $\frac{1}{2}\%$ Paniplus. The latter ingredient, no doubt, accounts for the high absorption. It is to be noticed that our best loaf occurs at one hour fermentation time.

Table VI shows results of the bake with a variation of fermentation time. Comparing the loaves produced at 0 hours and 1 hour fermentation time, we find a great improvement. Upon comparison of the loaves produced with 1 hour and 3 hours fermentation periods, we find a great decrease in the volume and quality. The period of production of good bread with this flour on a straight dough is very short, about 1 hour. The period over which a flour will produce good bread is the most vital factor of all and is one in which the baker has the greatest interest. By good bread I mean bread that a baker can sell without injury to his business, not the best loaf that can be obtained. For future reference I will call this curve of fermentation time against volume the straight dough curve.

¹ Arkady is the copyrighted name for a proprietary mixture of mineral yeast foods, such as ammonium chloride, calcium sulphate, sodium chloride, potassium bromate. Its action is that of so accelerating the fermentation of the yeast that considerable time or yeast may be saved.

² Paniplus is the copyrighted name of a patented gluten developer or dough conditioner, and is composed of a mineral peroxide and two inorganic phosphates. It differs from yeast foods in that its peroxide content causes the Paniplus dough to take considerably more water than a control dough. This is due to a swelling of the flour proteins as shown by viscosity measurements.

TABLE VI
RELATION OF FERMENTATION PERIOD TO BREAD PRODUCED FROM STRAIGHT DOUGHS

Ferments period hours	Volume of loaf, cc.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain	Texture	Absorption per cent
0	2740	F	P	G	F	F	F	68
1	3040	G	G	G	G	G	G	68
. 2	2840	G-	G	G	G	G-	G—	68
3	2840	G-	G	F	F	F	F	68
. 4	2690	F	F	F	F	F	F	68
. 5	2540	F—	F	F	F-	F	F	68
6	2480	P	P	P	P	P	P	68
8	2090	P-	P	P	P	P	P	68

This flour used with the same formula but in a sponge dough will give very different results. The straight line curve shown in Graph 3 is representative of doughs having sponge fermentation periods varying from 0 to 13 hours, with the dough time constant; namely, ½ hour. This shows a very gradual increase in volume as the sponge period is lengthened. Table VII gives the results of the entire bake.

TABLE VII

RELATION OF FERMENTATION OF SPONGE WITH CONSTANT DOUGH PERIOD TO BREAD PRODUCED

Fermenta Sponge hours	Dough		Spring in oven	Color of crumb	Color of crust	Flavor	Grain		Absorption per cent
0	0.5	2890	G—	G	G	G	G	G	68
1	0.5	2920	G	G	G	G	G	G	68
2	0.5	2990	G	G	G	G	G	G	68
3 -	0.5	2990	G	G	G	G	G	G	68
4	0.5	3060	G	G	G	G	G	G.	68
5	0.5	3050	G	G	G	G	G	G	68
6	0.5	3060	G	G	G	G	G	G	68
7	0.5	3100	G	G	G	G	G	G	68
8	0.5	3160	G	G	G	G	G	G	68
9	0.5	3200	G	G	G	G-	G	G	68
10	0.5	3240	G	G	G	G-	G	G	68
11	0.5	3300	G	G	G	G-	G	G	68
13	0.5	3340	G-	G	G	G-	G	G	68

Comparing the loaves produced at 0 and 4 hours sponge time, we find very little difference. A similar comparison of the loaves produced at 0 and 13 hours shows little difference. In fact, if these loaves were mixed indiscriminately it would be impossible for a bread expert to place them in the order of their fermentation periods. Thus it appears that we have a "leeway period," as the baker terms it, for making good bread of 13 hours with exactly the same flour that gave us good bread production of only 1 hour in the case of the straight dough.

If the dough period of the sponge had been varied, what would have been the effect? On the same formula, seven sponge doughs were given 4½ hours sponge fermentation time and then made into the dough stage and the dough period of fermentation was varied as

shown in Graph 3 by the dotted line. Comparing the bread by use of Table VIII we find a very great difference.

TABLE VIII

RELATION OF FERMENTATION PERIOD TO BREAD PRODUCED WITH SPONGE PERIOD CONSTANT

Ferment	ation peri	iod							
Dough hours	Sponge	Volume of loaf, cc.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain		beorption per cent
0	4.5	2840	G-	G	G	G	G	G	68
0.5	4.5	2900	G	G	G	G	G	G	68
1	4.5	2940	G	G	G	G	G	G	68
1.5	4.5	2790	F	G—	G	G	G	G	68
2	4.5	2690	F—	F	G-	G-	G-	G-	68
2.5	4.5	2590	P	P	F	F	F	F	68
8	4.5	2390	P	P	P	P	P	P	68

If we compare 0 hours with 1 hour, we find an improvement in the bread, while if we compare 0 and 3 hours, we find a great decrease in volume and quality. Examining the outside of the bread for the general characteristics of age, we find that between the bread obtained on the straight dough and that obtained by varying the dough time of the sponge dough, there is a great similarity—in fact the loaves are almost identical in their external appearance. Now comparing the bread obtained from the straight doughs with that of the variable sponge fermentation time and constant dough period, we find that there is a great deal of difference in their external appearance. The loaf obtained with 13 hours of sponge fermentation time showed none of the old characteristics as does the straight dough. If the sponge had been given some other time than 4½ hours and the dough time varied, a very similar curve would have been obtained. When a sponge is made into the dough stage it repeats the straight dough fermentation curve from then on. It is not the sponge fermentation time that must be watched so closely, but the dough fermentation time. In other words, it is the flour added at the dough stage that largely governs the character of the final bread. This governing action is of course materially decreased, as the percentage of sponge increases. The results reported are with a 60% sponge. Because of the similarity of the curves obtained from a straight dough, and the dough period of a sponge, where only one baking test can be made, there is no doubt that the straight dough method is the best, as the results so obtained are reflected in the dough period of the sponge.

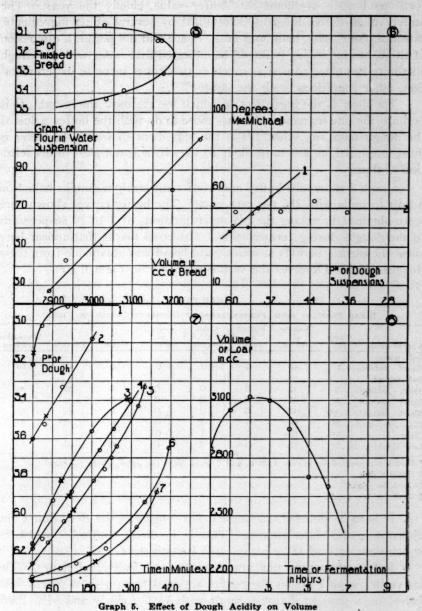
It is to be noticed that there is an increase in the volume of the bread obtained from a variation of the sponge time. This, it is believed, is due to the action of the acid upon the proteins of the flour. If gluten is exposed to the action of acid of varying concentrations and then added to a dough, we find that there is a great increase in the volume of the finished bread, as shown by the upper curve in Graph 4. The

volume increases as the amount of acid in the solution to which the gluten is exposed increases. When doughs are made by increasing the quantity of gluten not so treated with acid, there is a very slight increase in the volume of the finished bread, as seen by the lower curve in Graph 4. Again, if we suspend a flour in water containing a certain amount of acid and then add varying amounts of this flour to doughs, we find, in the lower curve of Graph 5, that the volume of the finished bread increases as the amount of added flour increases. Holding the percentages of flour constant, and increasing the acid, as shown in the upper curve of Graph 5, we find that the volume is increased up to a certain point, after which it again decreases. This is shown by the top graph which shows the pH of the finished bread plotted against the volume. All these doughs were baked as sponge doughs, that is, considering the quantity of flour or gluten exposed to the acid as the sponge or batter component of the dough. This seems to explain the increase in volume with increasing sponge fermentation.

If the viscosity is to run on the sponge during its fermentation period, we find from Graph 6, curve 1, that it increases in water suspensions as the acidity of the sponge increases, and that when the sponge is made into a dough this viscosity drops to its original value. That is to say, the salt added causes a reversal of the swelling of the gluten. There is no such increase in the viscosity of a suspension that is obtained from a straight dough, as shown by Graph 6, curve 2. It is believed that this action on the flour proteins and its reversal by the added electrolytes in the dough stage are responsible for the whiter crumb color obtained in bread made by the sponge dough process as compared with that made from straight doughs.

Summarizing, we can say there are two different actions of acids on doughs: (1) In sponge doughs there is a swelling of some of the proteins of the flour, which is largely reversed upon the addition of electrolytes, for example, salt, at the dough stage; and this action is responsible for whiteness of crumb color and other characteristics of a sponge, when compared with a straight dough. (2) There is an action of the acid upon the proteins of a dough which is responsible for the aging effect of the doughs, as shown by the increase in volume and other characteristics, the exact nature of which has never been ascertained by any investigator. The latter action is probably independent of enzymatic activity, as it is capable of being reversed by the addition of alkalies.

As the action of acid is so important, it is only natural that two factors must be considered: (1) The factors resisting an increase in acid formation, namely, the buffer value of the dough. (2) The



office and the contract of the

Graph 6. Relation of pH and Viscosity of Dough Suspensions

Graph 7. Acid Production with Different Grades of Flours During Fermentation

Graph 8. Straight Dough Curve of a Flour

force tending to overcome this buffer value, chiefly the yeast. The buffer value of the dough is determined by several of its ingredients, as water, flour, milk, malt, and salts. Space will not permit a discussion of these, but in passing it should be indicated that water with very high alkalinity has often caused as much as two hours increase in fermentation, other conditions being the same.

The flour is the ingredient in which we are most interested. It is perhaps the one ingredient that has more to do with the buffer value of the dough than any other. It is the ingredient in which the baker is most interested, as it is most likely to vary if he is not alert in his selection of flours.

Graph 7 shows the buffer curves of some straight doughs baked on a lean formula with 2½ per cent yeast. The buffer curves shown here were obtained by taking the pH determinations of 1 to 10 suspensions of the doughs during fermentation. The cross marks that appear here show the earliest periods at which good bread was obtainable from these doughs. Table IX gives the results obtained on these flours.

TABLE IX
BREAD PRODUCED FROM FERMENTATION OF DIFFERENT GRADES OF FLOUR

Kind of flour No.	Volume of loaf, cc.	Spring in oven	Color of crumb	Color of crust	Grain	Texture	Absorption per cent
Soft wheat							N. S. S.
Short patent1	G	· G	G	G	G	G	60
Soft wheat							
Short patent2	G	G	G	G	G	G	68
Short patent3	G	G	G	G	G	G	63
Short patent 4*	G	G	G	G	G	G	62
100 per cent5*	G	G	†	G	G	G	63
Clear6*	G+	G+		G	G	G	64
Low Grade7*	G—	G-	• •	G	G	G	64

^{*} Flours represented by curves 4, 5, 6, and 7 were from the same wheat mixture.

It is to be noted that this period is longest in the clear flours and shortest in the short patents. This is in direct contradiction to the conclusions arrived at by many other investigators.

Let us now turn our attention to some individual flours. The curve in Graph 2 shows the results obtained from a short patent flour baked on a straight dough formula with ½% Arkady and ½% Paniplus. Making use of Table VI and comparing the loaf produced at 0 hours and 1 hour fermentation time, we find a great improvement. On comparing the loaves produced at 1 hour and 3 hours, we find a decrease in both volume and quality of bread. The best bread occurred at 1 hour fermentation time and the fermentation time over which good

[†] Slightly dull.

[‡] Good for clear.

Good for low grade.

bread could be obtained is 1 hour. This flour required 1 cc. 0.1 normal lactic acid to bring 10 grams of it in 100 grams of water to pH 5, which we shall call its buffer value. It is the only flour about which we have had complaints from our plants.

TABLE X
RELATION OF BUFFER VALUE TO PERIOD OF GOOD BREAD PRODUCTION

Time of fermentation hours	Volume of loaf, cc.	Spring in oven	Color of erumb	Color of crust	Flavor	Grain	Texture	Absorption per cent
0	2850	F	F	G	G	G—	G-	68
1	3050	G	G	G	G	G	G	68.
2	3120	G	G	G	G	G	G	68
3	3100	G	G	G	G	G	G	68
4	2950	G-	G	G	G	G-	G-	68
5	2700	F	F	F	F	F	F	68
6	2650	F	F	F	F	F	F	68

Graph 8 shows the results of the bakes on another flour. Using Table X, we find that the best bread was produced in somewhere between 2 and 3 hours and that there was a period of good bread production of 2 hours. The amount of acid required to bring this flour to pH 5.0 was 1.7 cc. 0.1N lactic.

TABLE XI
RELATION OF BUFFER VALUE TO PERIOD OF GOOD BREAD PRODUCTION

Time of fermentation hours	Volume of loaf, cc.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain	Texture	Absorption per cent
0	2800	F	F	G-	F	G	F	67
1 .	8090	G-	G-	G	G	G	G.	67
2	3150	G	G	G	G	G	G	67
3	3150	G	G	G	G	G	G	67
4	3100	G	G	G	G	G	G	67
5	3000	G.	G-	G	G	G	· · · · · · · · · · · · · · · · · · · ·	67
6	2900	F	Dull	F+	G—	F+	F+	67

Graph 9 gives the results obtained on a third flour. With the aid of Table XI we find that the best bread occurred at somewhere between 3 and 4 hours. Furthermore, this flour has a period of good bread production of about 3 hours. This flour required 2.0 cc. of 0.1N lactic acid to bring it to pH 5.

In turning attention to a clear grade flour, from Table XII we find by comparison of the loaves produced at 2 and 3 hours, that the bread produced up to 2 hours was very small. Comparing the loaves produced at 3 and 8 hours, we find that at 8 hours this clear is still producing good bread. This gives it a period of good bread production of 5 or more hours. Its buffer value was 2.5 cc. 0.1N lactic acid (i. e., the amount of acid required to bring it to pH 5.0). The period of best bread production was somewhere between 6 and 7 hours. From Graph

10A, we see that there was a lag phase of about 2 hours in which the bread produced from this clear grade flour was exceedingly poor.

TABLE XII
RELATION OF BUFFER VALUE TO PERIOD OF GOOD BREAD PRODUCTION

Time of fermentation hours	Volume of loaf, ec.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain	Texture	Absorption per cent
0	2700	F	F	G	F	F	F	69
1	2720	F	F	G.	F	F	F	69
2	2750	F	F	G	F+	F+	F+	69
3	2900	G-	G-	G	G	G-	G—	69
4	8000	G	G	G	G	G	G	69
6	8200	G	G	G	G	G	G	69
6	8250	G+	G	G	G	G	G	69
7	8250	G+	G	G	G	G	G	69
8	8250	G+	G	G	G	G	G	69
9	8150	G	G	G	G	G	G	69
10	8100	G	G	G	G	G	G	69
11	8000	G—	G-	G-	G-	G-	G-	69
12	2900	G-	G-	F	F	F	F	69
13	2900	F	F	F '	F	F	F	69

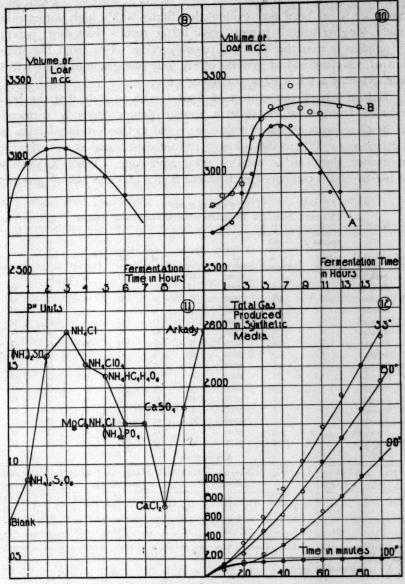
If this clear grade flour is baked with the same formula, but using the sponge dough, we obtain the results shown in Graph 10B. Here again we have a phase of poor bread production. Referring to Table XIII, beginning with 3 hours we have good bread which extends through 14 hours or more on the sponge dough. The buffer value of the flour was 2.5 cc. 0.1N lactic acid.

TABLE XIII

RELATION OF BUFFER VALUE TO PERIOD OF GOOD BREAD PRODUCTION WITH VARIABLE SPONGE
FERMENTATION

Time of fermentation hours	Volume of loaf, ec.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain	Texture	Absorption per cent
0	2840	F	F	G	G-	F	F	68
1	2890	F	F	G-	G-	F	F	68
2	2900	F	F	G	G-	F	F	68
8	2950	G-	G-	G	G-	F	F	68
4	3190	G	G	G	G	G	G	68
5	3290	G	G	G	G	G	G	- 68
6	8350	G+	G	G	G	G	G	68
7 .	8340	G+	G	G	G	G	G	68
	3470	G+	G	G	G	G	G	68
9 .	8340	G+	G	G	G	G	G	68
10	8820	G+	G	G	G	G	G	68
11	3315	G+	G	G	G	G	G	68
18	8850	G+	G	G	G	G	G	68
14	8340	G+	G	G	G	G	G	68

Other examples could be given but space will not permit. As a summary on flour, I have found that the buffer value of a flour is a good index of the fermentation period of a dough, other ingredients being constant. As the buffer value increases, the period of production of



Graph 9. Straight Dough Curve of a Flour Graph 10 A. Straight Dough Curve of a Clear Grade Flour

Graph 10 B. Curve Resulting from a Variable Sponge Fermentation and Constant Dough
Time on a Clear Grade Flour

Graph 11. Effect of Various Salts on Rate of Acid Production
Graph 12. Effect of Temperature in Yeast Storage on Gas Production

good bread from similar grades of flour seems to increase. From plant experience it has been very evident that flours with a high buffer value, namely, long or baker's patents, give better results than short patents. My opinion is that the day will possibly come when from the standpoint of economy and of general utility only one grade of flour will be made, possibly a 95 or 97% for baker's use.

Before leaving the subject of flour I wish to state that the bread produced from these clears in a sponge dough correctly fermented was in all respects except crumb color equal to that produced from the short patents. Where the color of the finished bread is not of prime importance, they can be used to great advantage. Table XIV shows the use of clears compared with patent flours in some bakery products.

TABLE XIV
BAKERY PRODUCTS PRODUCED FROM CLEAR GRADE FLOURS

Kind of dough	Time of sponge fermen- tation hours	Time of dough fermen- tation hours	Volume of loaf, cc.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain	Texture
Straight		4	8900	G	G	G	G	G ·	G
Straight		2.5	2900	G	G	G	G	G	G
Sponge	5	0.5	8300	G+	G	G	G	G	G
Sponge	3.5	0.5	2990	G	G	G	G	G	G
Straight		4	8000	G	G	G	G	G	G
Straight		2.5	.2950	G	G	G	G	G	G
Sponge .	5	0.5	3200	G+	G	G	G	G	G
Sponge .	8.5	0.5	8000	G	G	G	G	G	G
Sponge .	5.5	0.5	3250	G+	G	G	G	G	G
Sponge .	3.5	0.5	3020	G	G	G	G	G	G
Sponge .	7	0.5	3500	G+	G	G	G	G	G
		0.5	3275	G	G	G	G	G	G
		0.5	3600	E-†	G	G	G	G	G
Sponge .	5	0.5	3300	G	G	G	G	G	G
Straight		5.5	2600	G	G	G	G	G	G
Straight		8.5	2550	G	G	G	G	G	G
	dough Straight Straight Straight Straight Straight Straight Straight Straight Sponge Sponge Sponge Sponge Sponge Sponge Sponge Sponge Sponge Straight	kind of dough Kind of dough Straight Sponge .5 Sponge .3.5 Straight Straight Straight Straight Straight Straight Straight Straight Sponge .5 Sponge .5 Sponge .5 Sponge .5 Sponge .5 Sponge .7 Sponge .7 Sponge .7 Sponge .5 Sponge .5	Sponge Sponge Straight Sponge S	Kind of dough sponge fermentation hours dough of loaf, ex. Volume of loaf, ex. Straight 4 3900 Sponge .5 0.5 2990 Sponge .5 0.5 2990 Sponge .3.5 0.5 2990 Straight 4 3000 Straight 2.5 .2950 Sponge .5 0.5 3200 Sponge .3.5 0.5 3200 Sponge .5.5 0.5 3250 Sponge .3.5 0.5 3250 Sponge .5.5 0.5 3250 Sponge .7 0.5 3500 Sponge .5 0.5 3275 Sponge .7 0.5 3600 Sponge .5 0.5 3300 Straight .5.5 2600	Kind of dough fermentation hours Nolume Spring in oven	Sponge Fermentation hours Spring Color tation hours Spring Color tation hours Straight 4 3900 G G G Sponge 5 0.5 3300 G G G Straight 2.5 2990 G G G Sponge 5 0.5 3200 G G G Sponge 5 0.5 3200 G G G Sponge 5 0.5 3250 G G G Sponge 5 0.5 3250 G G G Sponge 7 0.5 3500 G G G Sponge 7 0.5 3600 E † G G Sponge 7 0.5 3600 E † G G Sponge 7 0.5 3300 G G G Straight 5.5 2600 G G G Straight 5.5 2600 G G G G Straight 5.5 2600 G G G G G G Straight 5.5 2600 G G G G G G G G G	Kind of dough sponge tation hours dough ferrmentation hours Volume of loaf, ce. Spring of oven of crumb Color of color of crumb C	Kind of dough sponge fermentation hours dough fermentation hours Volume of loaf, ec. Spring of orumb Color of orumb Color of orumb Flavor Straight 4 3900 G	Kind of dough sponge fermentation hours dough cathedral fermentation hours Volume of loaf, cc. Spring oven of crumb crust Color of crumb crust Flavor Grain Straight 4 3900 G

Loaf No.	rption er cent	(C)	No.	rption er cent	EDVIN TO	No.	rption er cent	Loaf	No.	rption r cent
1	 68	5		 67	9		 67	13		 66
2	 67	6		 65	10		 65	14		 65
3	 66	7		 67	11		 66	15		
4	 64	8		 65	12		 65	16		

^{*} All fermentation periods reported here are optimum periods obtained after a number of bakings.

Loaf No.

14

- 1-50-50* whole wheat bread produced by the straight dough process from a Northern clear.
- 2-Same as No. 1, but a patent flour used in place of clear.

[†] E- = Excellent minus.

^{*50-50} whole wheat: The first 50 refers to the percentage of patent or clear flour used relative to the total flour, the latter 50 to the percentage of whole wheat flour used.

- 3—50-50 whole wheat bread produced by the sponge dough process from a Northern clear.
- 4—Same as No. 3, but a patent flour used in place of clear.
- 5—50-50 whole wheat bread produced by the straight dough process from a Southwestern clear.
- 6-Same as No. 5, but a patent flour in place of clear.
- 7—50-50 whole wheat bread produced by the sponge dough process from a Southwestern clear.
- 8-Same as No. 7, but a patent flour used in place of clear.
- 9—75-25 whole wheat bread produced by the sponge dough process from a Southwestern clear.
- 10-Same as No. 9, but a patent flour used in place of clear.
- 11-Raisin bread by sponge dough process from a Northern clear.
- 12-Same as No. 11, but a patent flour used in place of a clear.
- 13—Raisin bread by the sponge dough process from a Southwestern clear.
- 14—Same as No. 13, but a patent flour used in place of clear.
- 15-Coffee cake from a Northwestern clear.
- 16-Same as No. 15, but a patent flour used in place of clear.

Turning our attention to some of the things that tend to overcome the buffer value of a flour, we find that there are many, such as yeast, added salts, and certain malts. Only two of these will be discussed. First, let us consider added salts. Graph 11 shows the rate of increase of hydrogen-ion concentration expressed in pH units per hour of doughs containing various salts. These are averages that have been obtained by many different trials in a straight dough at 80° with 2½% yeast. Graph 16 shows the results of two series of doughs run both with and without one of the salts that is very commonly found in yeast foods. Table XV shows a comparison of the two bakes. Series A contained this added salt while Series B did not. Comparing the two loaves produced at the end of 5 hours, it is evident that this acid-accelerating salt has shortened the correct fermentation period and at the same time the period of good bread production.

Let us consider the yeast. This is the most perishable ingredient put into a dough, hence it is only natural that we should expect variation in it from time to time. This variation is to some extent, no doubt, due to the temperature at which the yeast is kept. For example, four cakes of yeast received the same day were stored at 50°, 80°, 90°, and 100°F. At the end of 24 hours the gas production in synthetic media was determined on these. Bakes were also made on these at the end of 24 hours. The bakes were made on the same flour and under the same conditions and at the same time. Thus, from Graph 12 we find that

there is a steady decrease in the gas-producing power of the yeast stored for the same length of time as the temperature increases. Comparing these gas production curves with the pH determinations of the doughs containing the yeasts stored at the various temperatures, it is interesting to note how these two sets of curves arrange themselves. It suggests that the yeast is the agent in the dough that is causing acid production. If it were bacteria, the pH curve on the dough containing yeast at 100°F should change much faster than the others, providing the bacteria were present in the yeast. This is not the case. And further, it seems that the bacteria in the flour have not been very active, at least for the first few hours of fermentation. The bacteria of the flour over very long periods of 10 hours or more, may begin to have an appreciable influence.

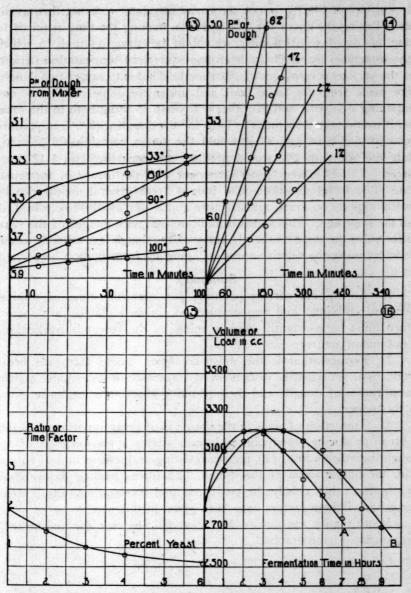
TABLE XV INPLUENCE OF AN ACID ACCELERATING SALT UPON THE PERIOD OF GOOD BREAD PRODUCTION

Time of fermentation hours	Volume of loaf, cc.	Spring in oven	Color of crumb	Color of crust	Flavor	Grain	Texture	Absorption per cent
			SE	RIES A				
0	2800	F	F	G	F	F	F	68
. 1	8100	G	G	G	G	G	G	68
2	8200	G	G	G	G	G	G	68
3	3190	G	G	G	G	G	G	68
4	3100	G—	G	G	G	G-	G	68
8	2950	F	G-	F	G-	F	F	68 -
6.	2870	F	F	F	F	F	P	68
7	2750	F	F	P	P	P	P	68
			SI	RIES B				
0	2850	F	F	G	F	F	F	68
1	8000	G-	G-	G	G	G	G	68
2	3150	G	G	G	G	G	G	68
3	8200	G	G	G	G	G	G	68
4	3200	G	G	G	G	G	G	68
5	3150	G	G	G	G	G	G	68
6	3100	G	G	G	G	G	G	68
7	2980	G	G	G	G	G	G	68
8	2800	F+	F+	F	F	F+	P	68
9	2700	F	F	F	P	F	P	68

In order to gather further information concerning the aging effect of yeast on doughs, the following experiment was performed: Doughs were made from the same flour under the same conditions with 1, 2, 3, 4 and 6% yeast, respectively, and fermented at 80°F. The pH of a 1 to 10 suspension of these doughs was run at the intervals shown. The following data were collected:

RATE OF DECREASE IN PH WITH VARYING YEAST PERCENTAGES

Yeast per cent	pH at end of 135 Min.		end of utes	pH at end of 220 Min.	pH at end of 270 Min.
1	6.1	186	6.08	5.9	5.84
2	5.91	186	5.73	5.66	
. 3	5.81	186	5.49	5.42	
4	5.665	192	5.35	5.26	
6	5.36	180	5.0		



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Graph 13. Effect of Temperature in Yeast Storage on the Development of Acidity in Doughs

Graph 14. Relation of per cent of Yeast to Rate of Acid Production in Doughs
Graph 15. Relation of per cent of Yeast to Activity
Graph 16. The Effect of an Acid-Accelerating Yeast Food

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On Graph 14, 3% is not shown, as the data were not then available. Taking the curve for 3% and then making the time required to bring this dough to pH 6 unity, we obtain the curve in Graph 15, which gives us factors by which to determine equivalent fermentation periods for the various percentages of yeast used. That is to say, if two doughs were made from the same flour and under the same conditions, one containing 3% yeast and the other 6% yeast, to bring both to the same age, it would take 0.56 times as long for the dough with 6% to produce bread of the same age, as it would the dough containing 3% yeast: while the one with 2% would produce the same bread in 1.42 times longer. This is in very good agreement with the theory of fermenta-The bread produced was judged from general appearance by several experts on bread manufacture and as far as could be told it all had the same age. This seems to indicate that with doughs of the same buffer value the slope of the pH curve of the dough is a valuable means of determining the relative speed of aging by fermentation.

Summary

- 1. Absorption, correct panning, pan greasing, time of mixing, speed of mixing, and temperature of finished dough, are factors which must be constantly kept in mind by the research worker and bread manufacturer.
- 2. Fermentation is the most important single factor in bread production. A scientific discussion of fermentation necessitates a strict classification of doughs and their resulting characteristics, as set forth in this paper.
- 3. The action of acids in the dough is of great importance. From a bread-producing standpoint, this necessitates a classification of the dough ingredients into, (1) factors resisting an increase in acid formation, the buffer value of the dough, (2) forces tending to overcome this buffer value, chiefly the yeast and acid accelerating salts. Measurements of these factors have been given in this paper.

Many thanks are due to Mr. Paul H. Sherrick for assistance in preparation of the graphs.

A STUDY OF WHEAT OIL'

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I. Introduction

The ether extract of all plants is composed in the major part of true fat, with smaller amounts of substances soluble in the fat or in the ether, such as phosphatides, pigments and sterols. Though the terms "ether extract" and "oil" are not quite synonymous they are often used interchangeably.

The amount of ether extract (which will be called oil or fat in this work) in the wheat kernel is about two per cent. This oil is not evenly distributed throughout the kernel, but is found most concentrated in the embryo and periphery cells with very little in the endosperm. In the periphery cells those of the aleurone layer seem to contain all the fat. Dividing the wheat kernel into three parts—the bran, the embryo, and the endosperm—Jacobs and Rask (1920) found the following amounts of fat:

		Per cent
Bran		5.6
Germ	· · · · · · · · · · · · · · · · · · ·	12.5
	endosperm	The second second

trin au

They state that all the fat of the bran occurs in the aleurone layer. Therefore, theoretically, patent flour should have about 0.75 per cent fat. This, however, is seldom the case as the fat content is more often about one per cent, showing that in milling the inner endosperm is contaminated with small quantities of either bran or embryo.

The oil obtained from these different parts of wheat has not been found to be identical, altho that from the aleurone layer, or bran, has been but little investigated. The oil extracted from the embryo has been designated as "wheat oil," and that from the flour as "wheat meal oil" or "wheat flour oil" (Lewkowitsch, 1915, ii; pages 174 and 293).

Owing to the small quantities of these oils in the wheat it has not been possible to extract a large percentage of the fat by pressure

¹ Condensed from a thesis presented by C. D. Ball, Jr. to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Master of Science, July, 1924.

This investigation was carried out in the laboratories of the Division of Agricultural Biochemistry, University of Minnesota, under the direction of Professor Ross Aiken Gortner as Major Advisor.

methods such as are used for the extraction of other oils. Consequently recourse has been had to various solvents. The "wheat oil" and "wheat flour oil" referred to in the literature are thus, in practically every case, the materials extracted by such solvents as ether or petroleum ether.

IL Historical

Many of the investigators who have worked on the oils of wheat have included in their work investigations on the oils of the other common cereal grains, namely, rye, barley, and oats. For this reason the historical part of this paper includes a summary of the work done on the oils of all these grains.

The first work recorded in the study of these oils is that on wheat by Toplet (1861), who found the phosphorus content of the fat to be 0.25 to 0.28 per cent.

Rittenhausen (1863) extracted the gluten of wheat and found that on driving off the ether, leafy crystals separated from the fat. These crystals were readily soluble in ether; only slightly so in absolute alcohol. From ether the crystals separated out as pearly plates. He obtained too small a quantity for identification but as it gave the color reaction for cholesterol he concluded that the material was cholesterol.

Kaiser (1864), in the study of barley fat, found it present to the extent of 3.0 to 3.5 per cent in the bran, and 0.8 to 1.0 per cent in the meal. The solid acids had a melting point of 57.5°. By analysis of the lead salts of the acids he stated that 80 per cent was palmitic and 10 per cent lauric.

Konig (1874), in a study of the fat of various plants, obtained the following information in regard to the fat of the seeds of oats and of rye:

	Oat oil	Rye oil
Oleic acid, per cent	60.5	91.6
Solid acids (stearic and palmitic), per cent	36.7	8.1
Glycerin, per cent	2.8	1.3
Melting point of solid acids	55-56°	57°

Stellwag (1886) separated the fat of barley by ether extraction. On standing, after driving off the ether, solid fat separated. This fat had a melting point of 13° and a saponification number of 182.7. He also determined the free fatty acids to be 13.62 per cent; neutral fat as 77.78 per cent; lecithin, as calculated from the phosphorus content of the fat, as 4.24 per cent; and cholesterol as 6.08 per cent.

The ether extract of wheat was studied by Schulze and Steiger (1889) in connection with the lecithin content of plant seeds. They

found that only a part of the lecithin could be extracted with ether. They suggested that the lecithin might be combined with other substances in a combination not affected by ether but decomposable by boiling alcohol. From the phosphorus content they calculated the lecithin content to be 6.51 to 7.29 per cent.

Stellwag (1890), in a study of the fats of various feed stuffs, extracted wheat bran, rye bran, barley, and oats with ether and benzene. The ether extracted more lecithin than the benzene. The fats from barley, wheat bran, and rye bran were similar in composition and composed of about three-fourths neutral fat, lecithin, and cholesterol. Oat fat contained a slimy substance. Determinations were made on both filtered and unfiltered fat. The lecithin content of the former was much less than that of the latter, being respectively 0.76 and 2.87 per cent. Possibly the slimy substance was largely lecithin. Other results of his work are recorded in Tables I, II, III, and IV.

TABLE I
CHEMICAL AND PHYSICAL CONSTANTS OF THE CILS OF WHEAT AS GIVEN BY
VARIOUS INVESTIGATORS

Investigator Date Part of wheat used	Stellwag 1890 Bran	Spaeth 1894 Flour	DeNegri 1898 Embryo
Specific gravity		0.9068(15°/15°)	0.9245 (15°/15°)
Refractive index		1.4851(25°)	1.4750
Saponification No		166.5	182.81
Iodine No		101.5	115.17
Reichert-Meissl No		2.8	
Hehner No			
Unsaponifiable, %			
Free acids, %	14.85		5.65
Melting point of solid acid	s, °C	84.0	89.5
Iodine No. of insol. acids			128.27
Neutral fat, %	78.78		
Total acids, %	89.71		
Molecular weight of fatty	acids 285.0		

Investigator Date— Part of wheat used	Frankforter and Harding 1899 Embryo	DeNegri and Fabris* and Plucker Flour	Alpers 1918 Embryo
Specific gravity	0.9292 (15°/15°)		0.9320(25°/25°)
Refractive index	1.48325 (20°)	1.4851	1.4766
Saponification No	188.83	182.8	180.0
Iodine No	115.64	96.1 to 112.5	122.6
Reichert-Meissl No		2.95 to 4.95	0.75
Hehner No			95.81

[·] Quoted by Lewkowitsch, Vol. 2, p. 240 (1909).

Spaeth (1894) extracted wheat, barley, and rye flours with ether and petroleum ether, drove off the ether, allowed the remaining oil to stand until no further material separated, and then filtered it. His results are recorded in Tables I, II and IV.

Oat fat was investigated by Moljawko-Wesotzki (1894), using petroleum ether as the solvent. He described it as brown in color, crystallized at -5°, had a specific gravity of 0.852. The Reichert-Meissl number was 0.9, which was due to formic and probably capylic and "caprinic" acids. The iodine number of the fat was reported as 62.8 and that of the fatty acids as 93.1. From oxidation by potassium permanganate the acids were concluded to be oleic and erucic. His results are summarized in Table III.

Spaeth (1896) found that fat of damp wheat flours showed a lower iodine number than that from normal flours; that drying the flour lowered the iodine number, and that long heating of the fat caused polymerization of unsaturated acids.

Wallerstein (1897) in studying the changes of fat in germination of barley gave a rather complete analysis of the crude fat from the barley kernel. The total fat content was 2.28 per cent. Other results of this work are tabulated in Table II.

TABLE II

CHEMICAL AND PHYSICAL CONSTANTS OF THE OILS OF BARLEY AS GIVEN BY VARIOUS
INVESTIGATORS

Investigator	Stellwag	Spaeth	Wallerstein
Date-	1890	1894	1897
Part of barley used	Seeds	Flour	Seeds
Specific gravity		0.9765 (15°/15°)	
Refractive index		1.4771	••••
Saponification No.	184.2	164.7	182.1
Iodine No.		95.2	114.1
Reichert-Meissl No.		0.80	0.031
Unsaponifiable, %	6.08	••••	4.7
Free acids, %	27.56		16.52
Melting point of solid acids, °C.		35.0	
Neutral fat, %			88.85
Total acids, %	86.88		
Molecular weight of fatty acids	286	• • • • • • • • • • • • • • • • • • • •	284.7
Ester No.			165.58

A study of the phytosterols of wheat and other grains was made by Burian (1897). He obtained two sterols from the unsaponifiable matter of wheat and of other grains. One he called sitosterol, and the other parasitosterol. These compounds differed in regard to melting point, crystalline form, and optical rotation from the substances isomeric with animal cholesterol, which substances had already been called phytosterols by Hesse, Benecke, and other workers. Both of these sitosterols of Burian's were given the formula $C_{27}H_{44}O$ plus H_2O . The specific rotations of sitosterol and parasitosterol were respectively -26.71° and -20.8° ; melting points 137.5° and 132.5° ; and melting points of their acetates 124.5° and 127.5°

De Negri (1898) investigated the oil of the wheat germ. From a total fat content of 125 grams he obtained by pressure 80 grams of oil, or 64 per cent. He described the oil as being soluble in ether, benzene, chloroform, and carbon tetrachloride; insoluble in cold anhydrous alcohol, but soluble in thirty parts of hot alcohol. At 65° it dissolved in an equal amount of acetic acid. He stated that the oil became rancid very easily. After a year the acidity had increased from 5.65 per cent to 43.86 per cent, calculated as oleic acid. Other results which he obtained are recorded in Table I.

TABLE III
CHEMICAL AND PHYSICAL CONSTANTS OF THE OILS OF OATS AS GIVEN BY VARIOUS
INVESTIGATORS

Investigator Date Part of oat used	Stellwag 1890 seeds	Moljawsko- wezotski 1894 seeds	Dubovitz 1918 shelled	Paul 1921 seeds
Specific gravity		0.852	0.9110	0.925
			(15°/15°)	(15°/15°)
Refractive index		1.4706 (15°)		1.4701
Saponification No.	184.2		180.13	189.8
Iodine No.		62.8	91.78	114.2
Reichert-Meissl No.		0.9		
Unsaponifiable, %	2.11		1.61	1.18
Free Acids, %	27.56			34.70
Melting point of solid acids, °C.				27.5
Iodine No. of Insol. acids		98.1		
Total acids, %	88.51			
Molecular weight of fatty acids	278			284.8
Neutral fat, %	61.60			64.0
Acid No.			62.11	68.90
Total insoluble acids, %				98.6

A very complete study of the properties of the oil of the wheat germ was made by Frankforter and Harding (1899). They found that the oil could be best extracted by ether. In addition to the solubilities as described by De Negri, the oil was found to be soluble in carbon disulphide and acetic anhydride, and fairly soluble in methyl alcohol. It was not a drying oil. During an experiment which ran seventy-five days the greatest increase in weight of the oil, per 100 grams, was 0.42 grams, which occurred at the forty-fifth day; while at the end of the period there was actually a decrease in weight from the original of 0.42 grams. Linseed oil in a parallel experiment increased in weight, the final weight being 8.43 grams greater than the original on the basis of 100 grams of the oil. The viscosity of the wheat oil was greatest at 20°, decreasing below that temperature probably because of the separation of solid glycerides. The refractive index of the oil as extracted from the germ was 1.47878 at 20°, but by redissolving the oil in ether and evaporating rapidly a certain amount of material could be removed,

while the sterols could be extracted with alcohol. The refractive index on this purified oil was 1.48325. The absorption spectra of the oil was somewhat similar to that of linseed and of corn in that bands were shown in different parts of the scale. The lecithin determined from the phosphorus content of the oil ranged from 1.96 to 2.03 per cent, assuming that lecithin is the dioleyl ester, or C₄₂H₈₄O₉NP. They identified the sterol present as the para-cholesterol which Reinke and Rodewald (1881) had obtained from Aethalium Septicum. By different methods the sterol content was found to be from 1.8 to 2.6 per cent. Glycerol, as determined by oxidation with potassium permanganate and subsequent determination of the oxalic acid produced, was found to be from 7.34 to 7.53 per cent. Other results of this investigation are recorded in Table I.

TABLE IV

CHEMICAL AND PHYSICAL CONSTANTS OF THE OILS OF RYE AS GIVEN BY VARIOUS

INVESTIGATORS

Investigator Date Part of rye used	Stellwag 1890 Bran	Spaeth 1894 Flour	Alpers 1908 Seed	Alpers 1908
	Bran			Embryo
Specific gravity		0.8769 (15°/1	5°) 0.9834	0.9322
Refractive index		1.4765		1.4774
Saponification No.	175.1	172.8	196.0 -	174.3
Iodine No.		118.5	81.8	127.7
Reichert-Meissl No.		0.88		0.88
Unsaponifiable, %	7.64			
Free acids, %	16.44			
Melting point of solid acids, °C.		86.0		
Total acids, %	93.75			
Molecular weight of fatty acids	285.6			
Neutral fat, %	78.31			
Hehner No.			88.8	96.01

Ritter (1902) criticized Burian's work on the sterols and obtained from wheat a single sterol with melting point of 136.5°, which corresponded to the sitosterol of Burian. This substance originally melted at 132° but by repeated crystallizations changed to 136.5°. The change to the lower melting point could not have been brought about by treatment of the sitosterol with alcohlic potassium hydroxide, as he found it was unaffected by such treatment.

Kosutany (1907, page 58), in his book on Hungarian wheat and flour, states that the lecithin from wheat fat is the disteryl ester rather than the dioleyl ester.

Gortner (1908), during an investigation of bleached flours, extracted oil from the flours with ether. On standing, white crystals separated which were oily to the touch, and which, after recrystallization from absolute alcohol, melted at 96.5°. The compound did not saponify, as shown by no change in melting point, before and after treatment with alkali. He believed the compound to contain nitrogen.

In a study of seeds of various plants, Schulze (1910) confirmed the presence of sitosterol in wheat kernel fat. He also observed the presence of a small amount of another substance similar in composition to sitosterol, but believed that it was identical with all the other plant sterols.

Power and Salway (1913) examined the residue obtained after saponification of the wheat germ oil. This residue, extracted with ethyl acetate, yielded a substance of melting point 138°, which contained 4.9 per cent of water of crystallization, and had a formula of C₂₇H₄₆O. They concluded it to be sitosterol. They also investigated the acids of the wheat oil. These were separated by the lead-salt-ether method, and the solid acids converted into their methyl esters. These distilled at 193-195° at 15 mm. pressure; had a saponification value of 205; and on decomposition yielded acids of melting point 63-64°. They concluded the solids acids to be stearic and palmitic in about equal proportions. The liquid acids practically all distilled at 245° at 25 mm. pressure; their neutralization value was 200.4 and their iodine number 167. From these data the authors concluded the liquid acids to be mainly linolic acid.

A new significance of the ether extract of the wheat kernel was suggested by Hart and McCollum in their nutrition studies (1914). They believed that the wheat embryo contained a toxic substance, which, however, could be removed by extraction with ether. Voegtlin and Myers (1918) disagreed with them, claiming that the so-called toxicity could be alleviated by a suitable salt mixture in the diet, and was not due to any material in the wheat embryo.

De Negri and Fabris, and Plucker, according to Lewkowitsch (1915, i, page 293) appear to have investigated the oil from wheat flour. Their results are tabulated in Table I.

Alpers (1918) studied the composition of the oil from the embryos of wheat and of rye, and the oil from the whole rye seed. He found the lecithin content of the oil to vary with the method of extracting the oil, crude rye oil had 3.04 per cent, crude wheat 2.7 per cent, lecithin. Other results of his work are recorded in Tables I and IV.

Oat oil received the attention of Dubovitz in 1918. He merely reported an analysis of the composition as obtained from shelled oats, This is recorded in Table III.

A very complete study of the sterol content of wheat was made by Ellis (1918), who confirmed the work of Ritter and obtained a sterol of melting point 137.5°, which gave an acetate melting at 127°. These coincided with the values for sitosterol. However, the bran yielded a substance of melting point 142°, which gave the cholesterol color reactions, and yielded an acetate of melting point 137°. She stated that mixtures of sterols had the property of crystallizing as if only a single compound were present.

Berry (1920) found that free fatty acids in oat oil were negligible, but hydrolysis occurred in proportion to the time elapsing between grinding and extraction. The effect of drying was to decrease hydrolysis but not to prevent it.

Paul (1921) extracted oats with petroleum ether and filtered the extract through kaolin and kieselguhr. On cooling, after driving off the solvent, the residue had become semi-solid owing to separation of a light brown mass which consisted almost entirely of lecithins. It was present to the extent of about one per cent of the extracted oil. The oat oil commenced to become gummy only after about two months, but if held at 99° a hard varnish was produced in two or three days. On keeping the oil closed for three months the acid value was little affected, but the odor was that of a rancid oil. Other results of his work are recorded in Table III.

While the work reported in this paper was being completed, Anderson and Nabenhauer (1924, 2) reported the presence of two sterols in what they called the "wheat endosperm." From wheat flour, by extraction with petroleum ether and then ether, they obtained from the unsaponifiable matter a crude sterol of melting point 138.5°, specific rotation in chloroform —15.6°. From wheat bran, however, they separated a substance which they imply was analogous to the crude sterol mentioned, but which was separated into levo and dextro rotatory fractions. The former had a specific rotation of —33.46 in chloroform, corresponding to sitosterol; the latter, after thirty-eight recrystallizations melted at 144-145° and showed a specific rotation of +25.82°. This they called dihydroxitosterol. It appeared to be identical with the substance obtained by them from corn (1924, 1).

III. Experimental

There was a two-fold object in making this investigation:

- 1. To compare the composition of the ether extract of the embryo and that of the ether extract of the flour.
- 2. To determine some of the properties of the material which separated out from wheat flour oil.

1. Ether Extract of the Embryo and of the Flour of Wheat

Materials Used.—The wheat embryos were obtained in large quantity in very pure condition from the Washburn-Crosby Mills, Minneapolis. Most of the embryos used had been extracted in the nutrition laboratory preparatory to extracting vitamin B.

The wheat flour used was of patent grade. One lot was milled in Michigan, but most was obtained from the Minneapolis mills.

Preparation of the ether extracts.—The apparatus used was a large porcelain extractor which held from two to four pounds of material. It was arranged for continuous extraction of all the wheat embryo oil and for a part of the wheat flour oil. Owing to the small quantity of oil in the flour it was quite difficult to get a sufficient quantity for investigation with this apparatus. During the latter part of this work, a Lloyd extractor became available. From twenty to twenty-five pounds of material could be extracted at one charge. This apparatus was much more efficient, causing very little loss of solvent and giving a greater yield of oil.

TABLE V
PHYSICAL AND CHEMICAL CONSTANTS OF THE WHEAT OILS

	I	Embryo	Oil (Ex	tracted)	F	our Oil	(Extra	cted)
Determination	I	II	III	Averag	e I	II	III A	verage
Specific gravity sample 1			0.9	2485 (25	0/10)		0.	96729
							(2)	8° /1°)
								0.97145
							(28	30/10)
Refractive Index (17.5°)				1.4686				1.4714
Saponification No.	183.91	183.93	184.54	184.13	159.49	160.77	162.49	
					159.63	159.23	163.54	160.86
Iodine No.	123.99	123.63	123.32	123.64	105.27	105.57	105.77	105.43
Iodine No. of insol. acids	128.58	127.85	127.90	128.11				
Iodine No. of liquid acids	145.93	146.01		145.97				
Unsaponifiable, %								
method (1)	3.51	3.51		3.51				
" (2)	3.67	3.65		3.66	2.35	2.67	2.50	2.51
Acid No. fresh oil	21.41	21.55		21.48				
after three years	34.94	34.99	35.08	85.00				
Hehner No.	93.94	93.48		93.71				
Neutralization No. of insol.								
acids	206.38	205.34	205.47	205.73				
Neutralization No. of solid								
acids	230.26	227.63		228.94				
Neutralization No. of liquid								
acids	202.97	202.34		202.66				
Mean mol. wt. of insol. acids				272.72				
Mean mol. wt. of solid acids				245.08				
Mean mol. wt. of liquid acids				276.85				
Ester No.				162.65				
Reichert-Meissl No.	0.46	0.49		0.475				
Polenske No.	0.26	0.24		0.25				

The extracts obtained after partial concentration in the extractor were then filtered to free them from particles of flour or foreign material. They were then freed from ether by heating in the presence of carbon dioxide gas, first, at a temperature just above the boiling point of ether, and finally at the temperature of boiling water, to remove any small amount of alcohol or water that may have been present.

The extract of the wheat embryo was then dried over anhydrous sodium sulphate. The oil obtained was perfectly clear, but after several weeks a small amount of material separated out in the bottom of the container. This material will be referred to later in the work.

TABLE VI YIELD OF OIL EXPRESSED FROM THE EMBRYO

100	Weight of embryos used, gr	
	Weight of oil obtained, gr 12.39	
	Per cent oil in embryos as determined by analysis 9.56	
	Weight of oil in embryos, gr 23.90	
	Per cent of oil expressed from embryos 51.80	

In the case of the extract of the flour, there separated at once on cooling, apparently an appreciable quantity of a crystalline substance which on examination under the microscope appeared to be needle-like crystals but on close observation were hexagonal plates. Several attempts were made to filter off this material by suction and by ordinary filtration but unsuccessfully. It was found most feasible to obtain a fairly complete separation either by diluting the oil with ether, or in the case of freshly extracted oil, by carrying the separation of the ether to the point at which on cooling, this material separated out. In either case the ether-oil solution was centrifuged, the supernatant liquid decanted, and the remaining residue treated with small quantities of ether until free from oil, as indicated by the absence of color in the supernatant liquid. The decanted ether-oil solution was freed from ether by heating in the presence of carbon dioxide, as described above.

TABLE VII
Some Chemical and Physical Constants on the Oil Expressed from the Embryo

Determination.	I	II	III	Average
Sp. gr. (25°/1°)				0.92140
Refract. Index. (28°)				1.4715
Iodine No.	127.85	127.87	127.85	127.69

On cooling, a further quantity of the same material separated. The oil was again centrifuged and the supernatant oil decanted. It was then dried for some time over anhydrous sodium sulphate. The oil, after

TABLE VIII
SEPARATION OF INSOLUBLE ACIDS

Determination	I	11
Weight of acids, used, gr.	19.6754	20.7129
Weight of "saturated acids," gr.	3.3545	3.6510
Iodine No. of "saturated acids"	22.41	32.46
Weight of unsaturated acids contaminating saturated acids,		
; calculated as oleic acid, gr.	0.2492	0.3609
Actual weight of saturated acids, gr.	3.1053	3.2901
Approximate per cent saturated acids	15.77	15.88
" " unsaturated acids	84.23	84.12
(by difference)		

standing, was not entirely clear, but centrifuging failed to clarify it further, so it was used in this condition for analysis. The material which separated out will be referred to later.

Preparation of Oil Pressed Out From the Embryo

A quantity, 250 grams, was subjected to a pressure of four hundred kilograms per square centimeter in a hydraulic press. The oil obtained was filtered. It was lighter in color than that obtained by ether extraction. No material separated out on standing.

Methods and apparatus.—The methods used for the determination of the chemical constants of the oils were those worked out or modified by Holland, Reed, and Buckley (1915), with the exception of a few cases where noted. The following is a list of the determinations made:

- 1. Specific gravity by means of a Sprengel's Pycnometer, and as directed by the Methods of Analysis of the Association of Official Agricultural Chemists (1920, page 173).
 - 2. Refractive index by use of an Abbe refractometer.
- 3. Saponification number.
- 4. Iodine number by Wij's method.
- 5. Reichert-Meissl number and Polenske using the same sample for both determinations.
- 6. Unsaponifiable matter, as described, and also by the official methods (1920, page 252).
- 7. Acid number, as described, and also by the method of Steele and Sward (1922).
- 8. Neutralization number of the insoluble fatty acids.
- 9. Hehner number, according to official methods (1920, page 247).
- 10. Mean molecular weight of the acids.
- 11. Ester number.
- 12. Approximate glycerol content.
- 13. Separation of the insoluble fatty acids according to the official methods (1920; pages 250 and 253). The ether soluble lead soaps were treated with hydrochloric acid (1:5), the ether solution was filtered into a flask, and the residual lead chloride washed with ether. For the analysis of these acids, portions of the ether solution were transferred to weighed flasks, the ether was evaporated by gentle heating in the presence of carbon dioxide, and the flasks were reweighed.
- 14. Separation of the hexabromide of linolenic acid by the method of Eibner and Muggenthaler (Lewkowitsch, 1915, i, page 573).

2. Investigation of the Material Separating Out From the Ether Extracts

It was mentioned that when the embryo oil had stood for several weeks a very small quantity of material separated. In the case of the flour oil a very appreciable amount immediately separated, as had already been observed by Gortner (1908).

In the case of the embryo oil, the material was filtered through ordinary filter paper, and washed with small quantities of ether. About 0.3 grams was obtained from 500 to 600 cc. of oil. No solvent could be found which readily dissolved this material. Ether and boiling alcohol had some effect. After several attempts at crystallization from alcohol, the material which appeared on cooling was amorphous. Tests for carbo-hydrates by the α -naphthol test, and for proteins by the biuret and Millon's reagent were negative. Hager-Salkowski and Liebermann-Burchard reactions (Lewkowitsch, 1915; i; page 270) for sterols were positive. No melting point was obtainable. At about 185° to 190° the material turned brown and apparently decomposed. It gave no test for nitrogen. The material was evidentally not identical with that obtained from flour oil by Gortner (1908).

As this substance from flour oil was found by Gortner to resist saponification as carried out in oil analysis, it was decided to investigate the unsaponifiable matter of the embryo oil. About 300 grams of the oil were treated according to the method of Holland, Reed, and Buckley (1916) for the determination of unsaponifiable matter. From the ether extract, crystals appeared. These were recrystallized a number of times from alcohol. The crystals obtained were in the nature of interlaying plates. A yellow oily substance separated from the first mother liquor on evaporation of the latter but no other crystalline material was found. The following melting points (uncorrected) were obtained on the recrystallized material:

4th	recrystallization	 132.0-132.5°
5th	recrystallization	 131.5-132.5°
6th	recrystallization	 131.5-132.0°

It gave immediate positive tests with the other reactions for cholesterol, which are given by phytosterols, namely, the Hager-Salkowski and the Liebermann-Burchard (Lewkowitsch, 1915, i: 270). It also gave the reactions "A," "B," and "C" for sterols given by Whitby (1923). The acetate was prepared by heating a quantity of the substance with acetic anhydride for several minutes, driving off the excess acetic anhydride, and recrystallizing twice from alcohol. The melting point was 125.5-126.0° (uncorr.) which corresponds to the acetate of the para-sitosterol of Burian (1897). No evidence of other crystalline material of lower melting point was obtained from any of the mother liquors,

therefore it was reasonable to believe that the material which separates out from wheat flour oil is not found to any appreciable extent in the ether extract of the wheat germ.

As described under the section, "Preparation of Ether Extracts," an appreciable quantity of material separated from the flour oil which was removed by centrifuging and washed with small portions of ether by contrifuging, until the supernatant liquid was colorless.

The residue, obtained from one lot of oil (Michigan flour), was then treated with a large quantity of absolute alcohol in which most of the material dissolved. The supernatant liquid was poured off and almost immediately on partial cooling, crystals appeared. These were recrystallized twice from absolute alcohol. Their melting point was 93.0-93.5° (uncorr.).

It was then found that this material could be best crystallized from ethyl acetate in which it was apparently more soluble in the hot, though less soluble in the cold, than in the case of alcohol. Therefore, a larger quantity of the material-that obtained from the extraction of the oil with the Lloyd extraction apparatus—was washed by centrifuging with small quantities of ethyl acetate after washing with ether as described above. Ethyl acetate could not be used first, as lecithin is quite insoluble in this solvent but soluble in ether. The residue after centrifuging and washing with cold ethyl acetate was boiled with 250-300 cc. of ethyl acetate, filtered, and the remaining residue treated with smaller amounts of ethyl acetate. From the first extraction there soon separated a large quantity of colorless crystals, consisting of irregular hexagonal plates. A small quantity separated from the second extraction, but practically none from subsequent extractions. There still remained a small quantity of amorphous material (about 0.13 grams), which on fusing with sodium and subsequent testing for nitrogen gave a slight prussian blue test, showing the presence of a small amount of nitrogen. This amorphous material also gave a biuret test and Millon's reaction. It is reasonable to believe that such a quantity of protein may have been extracted by the small amount of water in the ether.

The total quantity of crystallizable material obtained from the twenty-three pounds of flour was 1.9 grams, or about 0.018 per cent of the flour. About 1.5 grams was obtained in the first extraction with 250-300 cc. of ethyl acetate. This is designated as 1, and the recrystallizations of this as 1 (a), 1 (b), etc. The mother liquors from 1 were concentrated, giving on cooling a small quantity of crystals which were combined with 2, that is, with the crystals obtained in the second extraction with ethyl acetate. The recrystallization of this fraction is designated as 1.9 grams, or about 0.018 per cent of the first extraction with e

nated as 2 (a). The remaining mother liquors were concentrated and yielded a small amount of crystals designated as 3, and the mother liquors from this fraction a still smaller amount designated as 4. The melting points (uncorr.) of these fractions were as follows:

	Fraction		Fraction
	94.0-94.5°	2(a)	89.5-91.0°
Control of the Control of the Control	95.5-96.0°	3	89.0-90.0°
1(c)	96.0-97.0°	4	87.5-88.0°
1(d)	96.5-97.5°		
1(0)	96 0-96 5°		

From all of these crystallizations, except fraction 4, colorless pearly crystals were obtained, which when filtered by suction, adhered together in a paper-like form. Fraction 4 was more fragile and gave the sharpest melting point.

Because only between 1 and 2 grams of the material was obtained from the wheat flour, it was thought advisable to extract a large quantity of flour, 100 to 200 pounds, with the idea of obtaining sufficient to prepare in a state of purity. Anderson and Nebenhauer (1924, 2) have shown that thirty-eight recrystallizations were necessary to purify the dihydositosterol which they obtained from wheat bran. This work on the extraction of the large quantity of flour will be taken up shortly and reported in another paper.

Qualitative tests were made on fraction 1(d).

- 1. About 0.1 gram was treated with acetic anhydride and heated for about half an hour in a concentrated sulphuric acid bath at 130-135°. The excess acetic anhydride was driven off and the residue recrystallized from hot ethyl acetate. The crystals obtained had the same pearly luster and crystalline form, and melted at 96.5-97.0° (uncorr.). A second preparation gave crystals which melted at 95.5-96.0° (uncorr.).
- 2. Another 0.1 gram portion was heated for about half an hour with acetyl chloride in the presence of a small amount of anhydrous sodium carbonate. The material remaining after decantation and expulsion of the excess acetyl chloride was crystallized from hot ethyl acetate. It had the same appearance as the original material and melted at 95.5-96.6° (uncorr.).
- 3. The cholesterol color reactions, which had all been positive on the material obtained from the unsaponifiable matter of the wheat embryo oil, were next tried.
 - a. With the Hager-Salkowski reaction no color appeared at first, later a light cherry-red, and after about half an hour the characteristic color.

- b. The Liebermann-Burchard test was positive.
- c. Whitby's reaction "A" was positive at once.
- d. Whitby's reaction "B" was negative.
- e. Whitby's reaction "C" was negative.
- 4. The solubility of the pure substance differed quite markedly from that of the crude material that had been separated from the flour oil. This may have been due to some inhibitive effect of the small amount of protein material present. The pure material was fairly soluble in carbon tetrachloride, chloroform, ethyl ether, hot ethyl alcohol, and hot ethyl acetate; insoluble in glacial acetic acid and in concentrated sulphuric acid. In the latter it turned slightly yellow. It did not dissolve in sodium hydroxide.
- 5. About 0.1 gram was boiled for half an hour with alcoholic sodium hydroxide. The residue after recrystallization seemed unchanged, and gave a melting point of 97.0-98.0° (uncorr.). However, another sample boiled for five hours gave a substance of melting point 137.5° (uncorr.). This product gave all the cholesterol color reactions as enumerated above.
- 6. When boiled with dilute sulphuric acid for several hours, the solution cooled, neutralized with sodium hydroxide, and tested with Benedict's reagent, a negative test for sugar and other reducing substances was obtained.
- 7. When fused with sodium and the residue dissolved and filtered, tests for nitrogen, sulphur, or the halogens were negative. The presence of a large amount of carbon was indicated in the sodium fusion.
- 8. On the ignition of 0.1079 grams of the material in a porcelain crucible no ash was obtained.

IV. Discussion

Comparison of the Ether Extract of Wheat Embryo and That of Wheat Flour

These oils, using the term as synonomous with the ether extract, as had been stated by other workers, appear to be quite different.

In physical appearance the oil from the embryo is light in color, clear and limpid, while that from the flour darkens very readily on heating and is very viscous.

The specific gravity of the embryo oil is quite normal, being respectively 0.92140 and 0.92485 on extracted and expressed samples. That of the flour oil is rather surprising, namely, 0.97145 and 0.96729 on samples obtained respectively from Michigan and Minneapolis milled flours. Spaeth (1894) gave a similar value to barley oil, other-

wise the values obtained in this work are much higher than is the case in other vegetable oils.

The saponification numbers of 184.13 and 160.86 for the two oils are noticeably different, that of the embryo oil being around the normal value for vegetable oils. The value for the flour oil, 160.86, is quite different from the value given by De Negri and Fabris reported by Lewkowitsch (1915, ii for "weizenmehl," page 293), but agrees very well with that obtained by Spaeth (1894) on "weizenmehl." In the present work, the time of the saponification was varied, from one to two hours, in the six samples analyzed, but only slightly different results were obtained, within the range of experimental error in the determination, as the oil was quite dark in color.

The iodine value of the embryo oil agrees quite closely with that obtained by Alpers (1918), which was somewhat higher than those reported by other workers. The difference between the two oils is emphasized by these iodine values, being respectively 128.11 and 105.64. Lewkowitsch (1915, ii, page 410) classifies the embryo oil as semi-drying and the flour oil as non-drying.

The unsaponifiable values of 3.59 and 2.51 for the two oils appear to be remarkably high as compared to the corresponding value for other oils. This unsaponifiable matter consists chiefly of sterols and the ether-soluble decomposition products of the phosphatides, together with small amounts of pigment. The high value, however, is not so surprising when we note that Frankforter and Harding (1899) found from 1.8 to 2.6 per cent of sterols, and they and other investigators from 1.96 to 7.27 per cent of lecithin, about a sixth of which appears in the unsaponifiable matter as choline. The sodium and potassium soaps are slightly soluble in moist ether, a contamination which is eliminated by the method of Holland, Reed, and Buckley (1916), as they extract the dried residue after saponification with dry ether. However, the results of their method as compared with those of the wet extraction method (Official Methods, 1920, page 253) show little difference. On treating the unsaponifiable residue with distilled water and testing for soap phenolphthalein no pink color was obtained.

Another difference which exists between the ether extracts of the two oils is the crystalline material which separates from the flour oil. This material was observed by Rittenhausen (1864) and called cholesterol because it gave the color reaction in chloroform solution with concentrated sulphuric acid. The same result was obtained in this work but other properties characterizing it as a simple sterol were not obtained. Thoms (1897), and Lewkowitsch (1915, i; page 271) have found positive reactions with this test given by a number of substances,

such as terpenes, resin acids, and some gums. Therefore the sterol color reactions are not specific for sterols. Spaeth (1894) apparently disregarded the material entirely, working only with the clear fat.

The crystalline form of this material, as found by the writer, was identical with that described, namely, hexagonal plates, for several of the plant sterols. However, the important fact that acetylation does not seem to take place would eliminate it from being a simple sterol. The melting point, too, is very different from any of the sterols described, except coprosterol which is found in animal excrements. As pointed out by Ellis (1918), mixtures of sterols crystallize as if the mixture were a single compound. The melting point, according to Anderson and Nebenhauer (1924, page 2), is not so good a criterion for purity as is the specific rotation. It would seem at present as if a large number of different sterols exist in plants, altho there is the question of the purity of the substance described, as well as the possibility, as is true with cholesterol, that the treatment, perhaps during isolation, may effect some rearrangement within the molecule. example, dihydrositosterol, as prepared by Anderson and Nebenhauer (1924, pages 1 and 2) melted at 144-145°, while that described by Hauth (Lewkowitsch, 1915, i, page 276) melted at 175°. Both were prepared apparently from wheat. However, Winterstein and Smolenski (1909), in preparing wheat phosphatides, extracted the so-called starch-free wheat meal with alcohol and then with ether. They obtained in the ether-soluble part phytosterol, and on further concentration, a substance which melted at 91-92°. They surmised this to be a mixture of phytosterol and phytosterol esters and so saponified the material. From the residue they obtained crystals, representing about half of the original quantity, which melted at 124°. Anderson (1923) found phytosterol m. p. 88. -88.5° in corn pollen. In the present work when the material from the flour oil was saponified for half an hour there was no effect on the melting point, but when saponified for five hours a substance separated which melted very sharply at 137.5° (uncorr.) it gave the sterol color reactions of Whitby (1923) "B" and "C" which were not given by the material before saponification. The other sterol reactions, which had been positive on the original material, were still positive. The melting point, it will be noted, is exactly the same as the melting point of sitosterol. This fact, together with the positive sterol color reaction, would indicate that the material separating from the flour oil was an ester of sitosterol. However, further work is planned to obtain a much larger quantity of this substance in order to prove its identity. It is also contemplated to extract the oil from the

bran and determine whether the same material separates from the ether extract.

Additional Properties of the Embryo Oil

It is well known that the separation of the acids by the lead-saltether method (Official Methods, 1920; 250 and 253) is not an exact separation into saturated and unsaturated acids. Lead oleate is rather insoluble in ether and so contaminates the saturated acids. If the iodine value of the "saturated" acids is assumed to be due to oleic acid, the actual weight of the saturated acids may be calculated. By doing this the per cent of saturated acids in the two samples was found to be respectively 15.77 and 15.88.

The separation of the liquid acids was carried only so far as linolenic hexabromide was concerned. The melting point of this hexabromide was 162.0 (uncorr.). This value is lower than that given by Lewkowitsch (1915, i: page 569), but as the value for the tetrabromide is 113-114°, it is reasonable to believe that wheat embryo oil contains some linolenic acid.

De Negri (1898) gave results which showed a great increase in acidity of wheat embryo oil which had stood for one year, namely, from 5.65 to 43.86 per cent calculated as oleic acid. The results in this work are quite in contrast, the values being 1.15 and 1.76 per cent, the latter figure, moreover, being obtained after the lapse of three years. The Kreis test, as modified by Kerr (1918), gave only a faint pink color, and on diluting 1:4 with kerosene, no pink color. This shows that the embryo oil can be kept without undergoing marked hydrolysis or becoming very rancid. The oil had been kept well stoppered and in the dark during the three years.

V. Summary and Conclusions

- 1. Chemical and physical constants have been obtained on the oils which were extracted from wheat embryo and from wheat patent flour by ether, and also some constants on that obtained from wheat embryo by pressure.
- 2. So far as the writer is able to ascertain, this is the first time that constants have been determined on the oil extracted from patent flour, which would be almost entirely the oil of the inner endosperm.
- 3. Wheat embryo oil differs from wheat flour oil in the following characteristics: It has a higher saponification number, a higher iodine number, and contains more unsaponifiable matter, but has a much lower specific gravity than the flour oil.
- 4. The embryo oil extracted by pressure has a slightly higher iodine number than that extracted by ether.

- 5. A material separates out from the flour oil which is not found in the embryo oil. It contains no nitrogen, sulphur, or halogens. It has a melting point of 96-97° (uncorr.). It gives some of the sterol reactions, but is not an alcohol. On prolonged saponification it yields a substance with the same melting point as sitosterol, and also gives all the sterol color reactions. The material which separates from the flour is probably a sitosterol ester.
- 6. Wheat embryo oil has been kept for three years in a well stoppered bottle with only a slight increase in free acidity, and with the development of only a trace of rancidity (Kreis test).

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WHEAT AND FLOUR STUDIES V

PLASTICITY OF SIMPLE FLOUR-IN-WATER SUSPENSIONS¹

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Introduction

A study of the so-called viscosity of flour-in-water suspensions was undertaken by Sharp and Gortner (1923). They state that some of their suspensions were undoubtedly plastic even though they called them viscous in a rather loose use of the term. A part of their studies should be repeated, using equipment designed to determine the plasticity constants of the suspensions.

Bingham (1916) made an outstanding contribution to the laws of flow in showing the difference between viscous and plastic flow through capillary tubes.

True liquids exhibit viscous flow. When a given liquid is forced through a capillary tube at a definite temperature, the volume of liquid passing through the capillary in unit time is, within limits, directly proportional to the pressure producing the flow. The viscosity of a liquid is a constant which is independent of the force applied. For the same liquid, temperature, and capillary,

$$\frac{\mathbf{V}}{\mathbf{P}} = \mathbf{k} \tag{1}$$

Where V is the volume of liquid passing through the capillary per second, P is the pressure in grams per square centimeter used to produce the flow, and k is a constant. This relation was first shown by Poiseuille and is usually referred to as Poiseuille's law. This law holds for pure liquids, true solutions, and probably for some dilute suspensions in which the particles are not too large. As the concentration of the dispersed phase is increased, a point is reached at which the suspension ceases to flow as a viscous liquid and begins to flow as a plastic solid. In the flow of a plastic solid, the volume passing through the capillary in unit time is not directly proportional to the pressure. Poiseuille's law does not hold for plastic solids.

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A true liquid will flow no matter how small the force tending to produce the flow, provided the force is permitted to act over a sufficient interval of time. A plastic solid, theoretically, will not flow until the force applied to produce the flow exceeds a minimum value. The force which is theoretically just sufficient to start the flow is called the "yield value" and is a property of the suspension. Actually some flow takes place with applied forces less than the yield value, and various explanations have been offered to account for this flow.

After the force applied to produce flow has exceeded the yield value by a sufficient amount, and for greater forces up to probably an upper limit, the pressure-flow curve approximates a straight line. If the force representing the yield value is subtracted from the applied force, the volume of flow is proportional to this corrected force. For a given plastic solid, at a definite temperature, and using the same capillary we have:

$$\frac{\mathbf{V}}{\mathbf{P}-\mathbf{n}} = \mathbf{k}_{1} \tag{2}$$

Where V is the flow in cubic centimeters per second, P is the pressure applied in grams per square centimeter, and p is the yield value pressure in grams per square centimeter. k₁ is a constant.

The difference between viscous and plastic flow can perhaps be brought out more clearly by reference to Figure 2. The flow, in cubic centimeters per second, through a given capillary is used as the ordinate and the shearing force in dynes per square centimeter applied to produce flow is used as abscissa. The scale of the ordinate is 3888 times the scale of the abscissa. The lines labeled 7.93 and 14.54 represent the flow of viscous liquids, for the points all fall on straight lines and the lines pass through the origin of the axes. The curves labeled 20.13 to 32.71 show the results obtained with plastic solids. The lower points lie on a more or less curved line, while the upper points lie on a straight line. The yield value is given by the extension of the straight portions of the curves to the abscissa, and in the set of results labeled 32.71 it has a value of 1360 dynes.

Bingham and White (1912) give the following equation as expressing most accurately the flow of viscous liquids through capillary tubes.

^{*} Equations 1 and 2 hold experimentally only where all the energy is employed in over-coming the resistance in the liquid, i. e., with very narrow, long capillaries.

$$\eta = \frac{\pi \ g \ r^4 \ P \ t}{8 \ v \ (1 + \lambda)} - \frac{M \rho \ v}{8 \pi t (1 + \lambda)}$$
(3)

 $\eta = \text{coefficient of viscosity}$

g = gravitational constant

P = pressure in grams per square centimeter

t = time in seconds

v = volume of flow

r = radius of capillary in centimeters

l= length of capillary in centimeters

 ρ = density of the liquid

M = a constant whose value was taken as 1.12 by Bingham and White. $\lambda = a$ correction to be added to the length of the capillary to correct for the viscous flow outside of the capillary.

In the equation the expression

$$\frac{M \rho v}{8 \pi t (1 + \lambda)}$$

is used to correct for the kinetic energy of the liquid on emerging from the capillary. This correction is usually very small and approaches zero in the case of long narrow capillaries. In the flow of plastic solids it is customary to disregard this correction. Neither is it necessary to correct the length of the capillary for the resistance to flow outside the capillary. Thus the equation for plastic flow may be written

$$S = \frac{\pi r^4 g (P-p) t}{9.1 r}$$
 (4)

Where S is the consistency of the plastic solid—a term corresponding to the viscosity, η , of viscous liquids; and p represents the yield value pressure in grams per square centimeter. The only difference between the equation for viscous flow and that for plastic flow is the substitution of (P-p) in the latter for P in the former.

The reciprocal of the viscosity, η , is called the fluidity, φ , and the reciprocal of the consistency, δ , is called the mobility, μ .

In order to express the data graphically in terms which are supposedly independent of the dimensions of the capillary, the pressure in grams per square centimeter is changed to the corresponding shearing force. The shearing force, F, on the walls of the capillary is given by the equation

$$\pi r^2 Pg = 2\pi r 1 F$$

and expressing in terms of F

$$F = \frac{r P g}{2 1} \tag{5}$$

where g is the gravitational constant, in this case 980.4. As for a given capillary the values r, g, and 1 are constant, they may be grouped in a

numerical factor which, for the capillary used in this investigation, is

$$F = \frac{(0.07931) (980.4) P}{(2) (10)} = 3.888 P$$
 (6)

where 0.07931 centimeters is the radius of the capillary and 10 centimeters its length, the pressure, P, being expressed in grams per square centimeter. Thus with the capillary used in this work, the total shearing force applied, F, equals the total pressure applied, P, expressed in grams per square centimeter, times the factor 3.888; and in like manner the shearing force, f, corresponding to the yield value, is obtained by multiplying the yield value pressure, p, expressed in grams per square centimeter, by the factor 3.888.

The volume of flow was calculated in terms of cubic centimeters per second, thus.

$$\frac{\mathbf{v}}{\mathbf{t}} = \mathbf{V} \tag{7}$$

where V is the flow in cc. per second. Substituting equations 5 and 7 in equation 4 we obtain

$$S = \frac{\pi r^3 (F - f)}{A V} \tag{8}$$

As π , r, and 1 are constants for a given capillary, equation 8 can be further simplified for calculation to

$$S = \frac{K (F - f)}{V}$$
 (9)

where

$$K = \frac{\pi r^3}{4} \qquad (10)$$

which for this capillary has the numerical value

$$K = \frac{(3.1416) (0.07931)^8}{4} = 0.0003918$$

The equation used in the calculations of this paper now reads

$$S = \frac{0.0003918 \text{ (F-f)}}{V} \tag{11}$$

Bingham (1916), using clay suspensions and Booge, Bingham, and Bruce (1922) using paints, came to the conclusion that the mobility and the yield value when expressed in terms of shearing stress, were independent of the dimensions of the capillary. The work of Bingham and Green (1919) and some of the statements of other investigators cast some doubt on this point. If the size of the suspended particle is not sufficiently small when compared with the size of the capillary, the size of the capillary would affect the results. This has been shown by Rothmann (1914), using blood. Bingham (1925)

found that the mobility and yield value of emulsoids were not independent of the dimensions of the capillary.

The bending of the flow curves of plastic materials toward the ordinate, as in Figure 2, has received the attention of Bingham (1916), Green (1920) (1923), and Buckingham (1921). Buckingham derives an equation for plastic flow which differs from equation 8 in having 4/3 f in place of f.

While the equation given by Bingham has been criticized to some extent, it was thought advisable to use this equation in the calculations made.

Bingham and Durham (1911), in their study of suspensions of low concentration, found that the fluidity and the concentration of the suspension showed a linear relationship. Their data for clay suspensions extrapolated indicated that a concentration of 4 per cent by volume would have zero fluidity, for aquadag a concentration of 5.4 per cent by volume, for infusorial earth in water 13 per cent, and infusorial earth in ethyl alcohol 12 per cent. Bingham (1916) found that for another clay suspension the concentration of zero fluidity was 19.6 per cent by volume. He also found that when the yield values obtained for the various clay suspensions were plotted against the volume concentration the relation was linear, and that this line extrapolated to the concentration axis indicated that a suspension of 19.6 per cent by volume would have a zero yield value. Thus the suspension was thought to change from a viscous liquid to a plastic solid at a volume concentration of 19.6 per cent, as indicated by plotting either the yield values of the plastic suspensions or the fluidities of the viscous ones against the percentage composition.

Bingham (1922) extrapolated some of the fluidity concentration data of suspensions given in the literature to zero fluidity and found that the concentrations of zero fluidity varied greatly. Thus Oden's (1912) data for sulphur sols were found to indicate a zero fluidity of 25 per cent by volume; Richardson's (1920) data for Trinidad Lake asphalt suspensions in benzene, a zero fluidity at 24.6 per cent; Biltz and von Vegesack's (1910) data for "night blue," a zero fluidity at 9.2 per cent by weight; Woudstra's (1908) data for colloidal silver, a zero fluidity at less than 1 per cent; and Botazzi and d'Errico's (1906) data for glycogen suspensions, a concentration of zero fluidity of 27.5 per cent by weight using one viscometer, and 41 per cent using another.

The calculations by Bingham which are most pertinent to this paper are those made from the data of Lüers and Schneider (1920) from which he calculated that a malt flour suspension should have a zero fluidity at 17.6 per cent by volume, which is thus the concentration sup-

posed to correspond to the transition from viscous to plastic flow. The volume of the flour was calculated from the displacement of toluene, which indicated that the density of the malt flour was 1.4779. A per cent. of 17.6 by volume corresponds to a concentration of about 22 per cent by weight. Lüers and Schneider point out the possibility of error in using this density to determine the volume of the flour in the water suspension.

The data of Lüers and Ostwald (1919) on the viscosity of flourin-water suspensions were examined to see at what concentration their determinations indicate that the suspensions should have zero fluidity. They determined the viscosities with only two concentrations of flour in water; and as the fluidities of most of these mixtures together with that of water did not fall exactly on a straight line no definite extrapolation could be made.

These calculations indicate that in some cases either the data are not true fluidities or that the extrapolation of the fluidity concentration curve to zero fluidity does not give the true transition point from the viscous liquid to the plastic solid. Bingham, Bruce and Wolbach (1923), using lithopone suspensions in linseed oil, found that the fluidity or mobility curve did not tend to strike the abscissa (percentage concentration) at the same place as the yield value curve extended. They also found that the yield value curve is not straight in its lower portion, but bends toward the ordinate, which indicates that all suspensions show plasticity and only vary in a uniform manner at the higher rates of shear. This partially explains the divergency in some of the values obtained by extrapolating the fluidity curves to zero fluidity. Bingham and Hyden (1922) make this statement, "There is reason for believing that fluidities of colloidal solutions as ordinarily measured are really a function of the shearing stress and therefore apparent fluidities only."

It seems from what is now known that in a series of suspensions the transition from those suspensions which are fluid to those which are plastic is gradual, and that suspensions of relatively low concentration may show a yield value. The yield value of the more dilute suspensions is apparently in some cases not a linear function of the concentration. After the concentration exceeds a definite value, the yield value becomes a linear function of the concentration and this linear portion of the curve extended to the abscissa gives what might be called the theoretical limiting concentration between plastic and viscous suspensions. With our present knowledge it seems that this theoretical concentration at which the linear relationship between the yield value and the concentration of the suspension begins, can be

found only by determining the yield values for various concentrations and extrapolating the linear portion of the curve. It is apparent that the distinction between the flow of suspensions as viscous liquids and plastic solids, in some cases at least, can not be sharply drawn. It is probable, however, that this straight portion of the yield value percentage composition curve represents a definite property of the suspension, depending perhaps on such factors as the size of the particles, their floculation, hydration, and electrical charge.

The work of the different investigators indicates that different types of flow concentration curves may be obtained for (1) clay suspensions, (2) paints, and (3) nitrocellulose suspensions in acetone (emulsoids).

Bingham and Hyden (1922) found that a 1.39 per cent solution of nitrocellulose in acetone at 30°C. did not have a constant fluidity. They state, "It is probable that even a very dilute nitrocellulose solution behaves like a plastic material in that the fluidity is a function of the shearing stress." "The relation between mobility and concentration is by no means linear, the first addition of nitrocellulose being more effective than the later ones." The mobility was found to increase with temperature in a nearly, altho not quite, linear manner. A very interesting relationship was brought out in their work by the discovery that the yield value of a 7.708 per cent solution decreased in a linear manner with rise in temperature and that this solution exhibited no yield value at a temperature of 43°C. They point out that "this indicates the possibility of a colloidal solution becoming a true solution at this temperature."

Bogue (1922) used the MacMichael viscometer and operated it at different speeds to obtain different shearing stresses. He investigated the temperature at which gelatin solutions became plastic as an indication of sol-gel transformation. He found that the temperature at which gelatin ceased to show a yield value was affected by the presence of salts, by hydrogen-ion concentration, and by the concentration of the gelatin. He concluded from his studies that there was no definite temperature of sol-gel transformation but that the temperature varied with the conditions mentioned.

Since Bingham (1916) first devised the capillary tube method for studying plastic solids, other investigators have applied the method to various materials. Herschel and Bergquist (1921) and Porst and Moskowitz (1922) (1923) have applied it to starch pastes; Bingham and Green (1919), Green (1920) (1923), Bingham, Bruce, and Wolbach (1923), and Bingham and Jacques (1923) to paints; Wilson and Hall (1922) and Hall (1923), to clay strips. The MacMichael vis-

cometer was used to study plastic flow in carbon suspensions in oil by Perrot and Thiessen (1920) and in gelatin by Bogue (1922). Other methods have been used for rubber by Marzetti (1923) and Williams (1924). Marzetti (1923) also used his method on bread dough, for he states that dough follows the same plastic flow law which he found for rubber—that is, the flow bears a relationship to the square of the force.

This investigation was undertaken to determine at what concentration a simple flour-in-water suspension becomes plastic. This object was accomplished by determining the yield values of suspensions of various concentration and plotting them against the percentage composition and extrapolating to the percentage composition axis. As previously mentioned, this is perhaps a hypothetical value in some cases, yet it probably represents a definite property of the suspension system.

Apparatus

Bingham (1916) (1922) and others have described rather elaborate and costly apparatus for the determination of plasticity. A much simpler and probably sufficiently accurate apparatus and one considerably less costly was constructed for use in this work. It is illustrated in Figure 1. "A" represents a galvanized iron tank of about 6 gallons capacity which was made by a local tinsmith from No.16 gage galvanized iron. An ordinary hand pressure pump, B, was connected to the tank by a piece of pressure rubber tubing. A bicycle tire valve was soldered to the tank for the intake valve. The compressed air was led from the tank to the plastometer by means of glass and pressure rubber tubing. At the point C in the air pressure line a T tube containing a glass stopcock was introduced to permit the escape of air when desired. Another T tube was introduced into the pressure line and connected to the mercury manometer, D. This manometer was so constructed that the pressure could be determined by measuring the difference in height of the levels of the mercury in the U tube by means of a meter stick. The U tube had a jog about midway in the arms, and the amount of mercury was so adjusted that both levels of the mercury could be read on the scale on one side of the meter stick. The meter stick could also be moved up and down in the support.

The plastometer was connected to the pressure line by means of a well-ground glass three-way stopcock, E, with two openings on one side and one on the other. When turned in one direction the plastometer was connected to the air of the laboratory, and when turned in the other direction it was connected to the air pressure line coming

from the tank A. The plastometer, F, consisted of a piece of glass tubing with an internal diameter of about 2.4 cm. and a length of about 9.0 cm. One-hole rubber stoppers were placed in the top and bottom, through the hole in the rubber stopper in the top a short piece of glass tubing was introduced to connect the plastometer to the three-way glass stopcock, and through the stopper in the bottom a capillary glass tube 10.00 cm. long was inserted. The inner ends of the glass tubes were just even with the inner ends of the stoppers. Two pieces of wood to keep the stoppers from blowing out were placed at top and bottom. The pieces of wood were pierced by three holes and were held

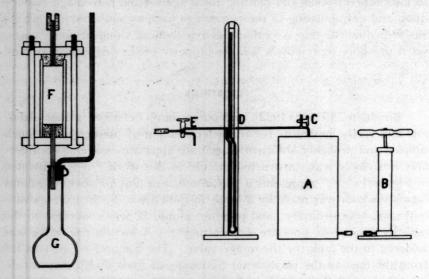


Fig. 1. Apparatus Used to Determine the Plasticity of Flour-in-Water Suspensions

in place by two long bolts. The plastometer was filled by removing the upper stopper. The material, after flowing through the capillary, was collected in a 25 cc. volumetric flask, G. The neck of the flask was calibrated so that the volume of flow could be read. The volumetric flask was connected to the lower end of the capillary by means of a two-hole rubber stopper, through one hole of which was introduced the capillary and through the other a piece of glass tubing long enough to reach up past the top of the plastometer. The whole plastometer could be placed in a water bath. A piece of capillary tubing of fairly uniform bore was selected by measuring the length of a mercury thread. The radius of the capillary was determined by measuring the length of a mercury column in the capillary, weighing the mercury, and looking up the corresponding radius in the table

given by Bingham (1922). The capillary used had a radius of 0.07931 centimeters. The length of the capillary was made as nearly as possible 10.00 cm. The average hydrostatic pressure level of liquid in the plastometer was found to be 13.4 cm. This value multiplied by the density of the suspension gives the hydrostatic pressure of the suspension in grams per square centimeter tending to produce flow. To this value was added the pressure in grams per square centimeter exerted by the air pressure line, that is, the height of the mercury column in the manometer multiplied by 13.544 for a laboratory temperature of 20°C. The sum of these two pressures gives the total pressure in grams per square centimeter tending to produce flow. Bingham (1922) gives a table for converting the heights in centimeters of mercury in the manometer into pressure in grams per square centimeter. The additional data necessary for the calculations are the volume of flow in cubic centimeters and the time of flow in seconds as determined by a stop watch.

Experimental

Sharp and Gortner (1923) pointed out the difficulties in obtaining reproducible results in their study of the so-called viscosity of flourwater suspensions, especially in the use of the capillary viscometer of the Ostwald type. After several preliminary trials with smaller capillaries, one with a relatively large radius (0.07931) was chosen. The results obtained with the smaller capillaries were not uniform, owing to plugging. Even with the capillary used, difficulty was encountered in obtaining concordant results with suspensions prepared in duplicate. It was found in a series of preliminary experiments that by shaking the suspensions uniformly for a definite period of time more concordant results could be obtained than when the attempt was made to determine the values without shaking. In order to make the mechanical treatment as nearly uniform as possible before making the determination, each suspension was prepared by placing the weighed amount of flour in a 500 cc. Erlenmeyer flask; the flask was placed for about 30 minutes in a water thermostat kept at 25°C.; 100 cc. of distilled water of a temperature of 25°C. was then added, and the flask was rotated to produce a suspension. The flask was then shaken in an excursion mechanical shaker for exactly 30 minutes. The mechanical shaker was enclosed in an air thermostat kept at 25°C. At the end of the shaking period the flow was determined on four aliquots using different pressures. The flask, in the meantime, was kept in the water thermostat. The four determinations were made as rapidly as possible, the time for making all four determinations never exceeding 25 minutes. The

determinations made from the aliquots of each flask were not made at consecutive pressures as represented in the curves in Figure 2, but the pressures applied were so varied that an aliquot from each flask was caused to flow at a pressure of sufficient magnitude to make the points fall on widely different places on the curve. The results are presented graphically in Figure 2. The points which apparently fell on the straight portion of the curve are indicated by a black center. The data for the points indicated by the black center were used to determine the tangents of the angle between the lines and the abscissa. The yield value was calculated by the method of least squares.

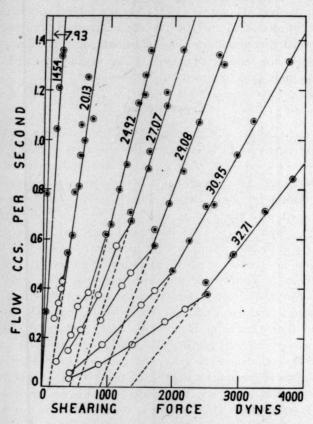


Fig. 2. Flow in Cubic Centimeters per Second Plotted Against the Force Producing the Flow, Using Flour-in-Water Suspensions Containing Various Percentages of Flour (Dry Basis)

As the equation for a straight line can naturally be used for the straight portion of the graph, we have the expression

(cc. per sec.) =
$$a + (dynes per square centimeter)b$$
 (12)

Where a and b are constants, b representing the tangent of the angle between the straight portion of the curve extended and the abscissa, and a the value in cc. per second when the shear in dynes per square centimeter is zero. The yield value, f, can be determined from these two constants

$$f = \frac{-a}{-b} \tag{13}$$

As the constant b of the equation (12) is the tangent of the angle made by the straight line with the abscissa, it represents the best value

for the ratio of
$$\frac{V}{F - f}$$
.
$$b = \frac{V}{F - f} \qquad \text{or} \qquad \frac{1}{b} = \frac{F - f}{V} \qquad (14)$$

and substituting the value for $\frac{F-f}{V}$ in equation 11 we obtain the

value for the consistency, 5

$$S = \frac{0.0003918}{b} \tag{15}$$

where b is determined either by the method of least squares or graphically. If b is determined graphically, the ratio of the numerical scale of units used in plotting must be taken into consideration. The scale of the ordinates in this case is 3888 times the scale of the abscissa, so the value of the tangent obtained from the graph must be divided by 3888. The constants for the straight portions of the curves as determined by the method of least squares and also the values of the constants as determined graphically are given in Table I. The values determined graphically agree fairly well with those determined by the method of least squares.

The data in Table I are expressed graphically in Figure 3. The abscissa represent the percentage composition of the mixture on the weight basis. The ordinates represent the yield value, the consistency, and the mobility.

The extension of the yield value curve to the percentage composition axis in Figure 3 intersects the base at about 19 per cent, thus indicating, in the case of this particular flour, that flour-in-water suspensions of a composition of 19 per cent or more of flour by weight, are plastic. As previously mentioned, the data of Lüers and Schneider (1920) as recalculated by Bingham (1922) indicate that a malt flour suspension became plastic at a weight concentration of slightly less than 22 per cent. There is no indication in these data of the yield value curve bending toward the ordinate. The logarithms of the concentra-

tion were plotted against the logarithms of the consistency and it was found that the points represented by concentrations from 14.54 to 29.08 per cent fell on a straight line, but the points corresponding to the other three concentrations fell in such places as to indicate that the consistency values were correspondingly higher than those which fell on the straight line. The fluidities of the more dilute suspensions are probably considerably in error and it can not be definitely determined from these data whether or not they fall on a straight line. The indi-

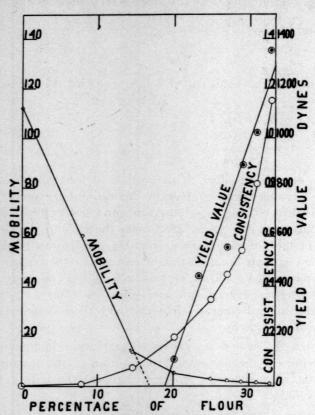


Fig. 3. Yield Values and So-called Mobilities and Consistencies Plotted Against the Percentage Composition by Weight (Dry Basis)

cation is that they do, altho this depends on the determination of one point only. If the fluidities of the lower concentrations fall on a straight line in Figure 3, the plot of the logarithms of the so-called consistencies of these points should not fall on a straight line.

The flow of water, 7.93, and 14.54 per cent suspensions were corrected for kinetic energy loss, which was considerable, especially in

TABLE I FLOW DATA FOR SIMPLE FLOUR-IN-WATER SUSPENSIONS OF VARIOUS CONCENTRATIONS

cy, Mobility les Los Z	112.0	60.2	13.6	6.2	2.9	2.2	1.8	113	6.9	
Consistency, Z z using values from equation	0.0089	0.017*	0.074	0.194	0.848	0.449	0.544	0.812	1.189	
Yield value, f, defermined graphically			0.0	109.0	489.0	660.0	894.0	1019.0	1360.0	
Yield value, f, determined from equation			8.9	+108.0	446.0	656.0	890.0	1019.0	1852.0	A DIED A ABI A A ATO
Constant, b, determined graphically			0.005512	0.002019	0.001102	0.0008650	0.0007279	0.0004804	0.0008436	A DATED O ADD
Constant b, from equation			0.004979	0.002019	0.001124	0.0008724	0.0007202	0.0004827	0.0003439	The second of th
Constant a, of equation			+0.0284	-0.2079	-0.5009	-0.4861	-0.6418	-0.4921	-0.4648	-
Moisture- free flour in suspension on weight basis per cent	0	7.98	14.54	20.18	24.92	27.07	29.08	80.95	82.71	Contract of the state of
Air dry flour added to 100 cc. water gms.	0	10	20	80	40	45	90	99	. 09	

the first two cases. It is doubtful whether the correction equation applies with any considerable accuracy where it forms so large a part of the total reading. The error in determining the rate of flow was very great for these low concentrations. While the value for water given by the corrected viscosity is fairly close to the true value, the results obtained with a 60 per cent sucrose solution did not show such good agreement, the average error being 7.2 per cent. The error introduced by disregarding the kinetic energy correction in the more concentrated suspensions was probably less than the experimental error in preparing the suspensions.

It is not known whether the flow constants of flour-in-water suspensions are independent of the dimensions of the capillary. The volumes of flow per second recorded in Figure 2 are larger than have usually been used in plasticity measurements, altho because of the large radius of the capillary the rates of shear were comparable with those used by other investigators. From the work of Lüers and Ostwald (1919) and Sharp and Gortner (1923) flours would be expected to differ somewhat in the concentration of the suspension marking the limit between viscous and plastic flow.

This investigation was limited to the study of simple flour-inwater suspensions. Suspensions of flour in water to which lactic acid has been added, producing an imhibition of the glutenin, become plastic at much lower concentrations than do those to which no acid has been added.

Conclusions

An apparatus is described for studying the plastic flow of fairly concentrated suspensions.

A particular flour-in-water suspension was found to be plastic when it contained 9 per cent or more of flour by weight on the dry basis.

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METHOD FOR A GRAPHIC RECORD OF TEXTURE, VOLUME, AND CONTOUR OF CAKES¹

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In experimental food work one of the chief difficulties encountered is to find ways and means for competently judging products made from day to day. When many products are prepared it is inconvenient to have photographs made and one cannot carry in mind the various qualities which are necessary to be judged. There are few graphic and mechanical methods for judging and there is great need for such methods.

In connection with a problem being carried out, "A Study of the Physico-chemical Properties of Cakes and the Ingredients of Cakes and their Relation to Each Other" the matter of judging was especially studied and considered.

Standard for Cake

The standard decided upon for a plain cake was as follows: A plain cake should be golden brown in color; slightly rounded on top; crust not sugary; crumb moderately fine, light, and moist; flavor pleasing and well blended.

Score Card for Cake

To judge according to this standard the following score card as proposed by Allison (1914) was used:

General	Appearance
	Color 5
	Size 5
	Shape 5
Flavor	•••••
Crumb	
	Texture 10
	Lightness
	Moisture 10
	Color 5
Crust .	•••••

In using this score card the personal element entered to a great degree and it gave no method for real comparison of the cakes made

100

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² Work in progress in Division of Home Economics, University of Minnesota.

from day to day. It was thought that a mechanical method should be used. So in addition to the scoring of cakes by means of the score card the specific volume of each cake was determined, using the method developed by Jackson (1914).

Prints of Cakes

In order that a graphic method might be used, prints of a slice of each cake were made. An article by Mohs (1924), "Size of the Pores in Baked Bread," gave the idea for the method of preparing the prints.

The following is the method used: Mix together thoroly equal parts of mimeograph ink, glycerine, and water. (If the ink is thin, the water may not be necessary.) Cut a piece of blotting paper slightly larger than the piece of cake of which a print is to be made. Allow the blotter to absorb all the ink mixture possible by dipping one surface into the mixture. Place this, ink side up, on a board and work the ink into the blotter with a camel's hair brush. By means of thumb tacks stretch tightly a piece of thin, soft, smooth, even-textured cloth over this. Allow it to stand from 5 to 10 minutes to absorb ink. More ink may have to be added after stretching the cloth, but before using the ink must be evenly distributed on the blotting surface and all excess ink wiped off or the print will be uneven.

Cut a piece of cake, ½ to ¾ inch in thickness, with a clean cut surface. Using the slice of cake as a stamp and the blotter as a pad, place the cake on the blotter, press lightly with the tips of fingers over the entire surface in order that every cell may have a film of ink. Transfer the cake to the paper on which the print is to be made. Again use finger tips to make sure that every portion of the slice has touched the paper. Great care must be used in placing the cake on the paper and again in removing it in order to secure a clean-cut picture rather than a blurred one. After making each print the blotting surface should be brushed clean. Add new ink as necessary, but never have an excess. Ordinary mimeograph paper serves the purpose, but a grade known as "Wedding Kid" bristol board gives the best results.

Specimens of prints are given in Figure 1.

Value of Prints

The prints have been of value in keeping a record of various types of cake made. They are not used as score cards as in bread, but simply as a means for comparing the cakes made with different variants. It has been found that the grain, the volume, and the contour of cakes are easily judged by means of the prints. The prints are especially valuable when used in connection with the specific volume of the

cake and it has been found that this graphic method in connection with a mechanical one has given a much more definite and accurate method of judging cakes, muffins, and like products than was previously available.

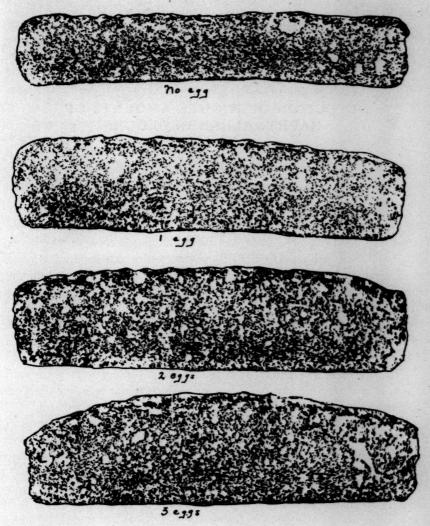


Fig. 1. Effect of Egg in Plain Cake

The variant in this series was egg, all the other factors were kept constant.

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DETECTION OF MINUTE AMOUNTS OF NAPHTHALENE IN FLOUR

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The writers had occasion to prepare testimony for a recent litigation in which it was alleged that flour which had been stored in a warehouse, had been rendered unfit for use by having become contaminated with napthalene which was used to protect other articles in the warehouse against damage by moths. It is quite obvious that naphthalene would not be knowingly applied to flour, yet it might be argued that naphthalene having a high vapor pressure, an appreciable quantity of it might have volatilized into the atmosphere. Further, it might be surmised that the flour could then adsorb this naphthalene vapor out of the air.

In any case, regardless of whether these suppositions were valid or not, it became necessary to ascertain with certainty whether the flour in question contained naphthalene and if possible in what amount.

The odor could be taken into consideration, but only as a presumptive test: first, because there are substances other than naphthalene which resemble it in odor and which could be mistaken for it, especially in high dilutions, of the order of magnitude of several parts per 100,000 parts of flour, which were to be dealt with in the case at hand; second, because odors in flour are known to be misleading as to their cause or origin. A case in point is the experience of Kuhl¹, in which instance the flour had the odor of phenol, which, it was thought, came from phenol used in disinfecting the flour mill against insect pests. Careful analytical work showed, however, that no phenol, so far as could be determined by the most delicate tests, was present. It is

¹ Chemiker Zeitung, Vol. 47, (1923) pp. 693, 807.

therefore evident that an odor test should by all means be confirmed in some other way, preferably by a definite, characteristic, chemical test.

Two very sensitive tests for naphthalene are first, the blue reaction product obtained when naphthalene reacts with formaldehyde and sulphuric acid² and second, the violet color resulting from the interaction of a chloroform solution of naphthalene with anhydrous aluminum chloride.³ Preliminary tests indicated that the latter was more sensitive and it is this test that was used throughout the work reported herein.

As stated, these tests had already been described, but it was necessary to work out a method of removing the minute amounts of napthalene from the flour in a form such that the tests could be applied. Various methods of extraction with suitable solvents as well as other modes of attack were abandoned one after another, in favor of the steam distillation method described below.

In spite of negative results obtained by the "chemical" method in certain cases, the problem still remained of reconciling the presumptively positive tests obtained by the odor method. That is, there were instances in which the odor seemed to indicate the presence of napthalene, whereas "chemically" its absence could not be contraverted. This apparent discrepancy was cleared up by determining, as closely as possible, the limits of sensitiveness of the odor and chemical tests and interpreting the results in this light.

These tests, when carried out by the procedures described below, have limits about as follows:

			o parts	of flour
"Chemical"	test	 1	to 1.5	parts
Odor test .		 3	to 5	parts

To obtain these test limits, mixtures were prepared of wholesome wheat flour and naphthalene in decreasing proportions and submitted to the tests. The point was then noted at which the positive response first vanished.

A consideration of the figures given above will make it evident that a suspected flour which smells of naphthalene and the odor of which is due to naphthalene will easily respond to the "chemical" test. Whereas in the case of a flour which smells of naphthalene but which fails to give a positive response to the "chemical" test, it may be concluded with certainty that naphthalene is absent and that the odor is due to some substance other than naphthalene.

² Chemiker Zeitung, Vol. 31, (1907) pp. 445, 486-87.

³ Mulliken, "Identification of organic compounds," published by John Wiley and Sons, New York, (1904) Vol. 1, pp. 176, 196-97.

Procedure for Detection of Naphthalene

Odor test.—(An adaptation of the procedure given by Jago).⁴ Moisten 50 grams of the sample, in a mason jar, with 30 cc. of distilled water. Close. Keep in an incubator at 37.5°C. for 2 hours. Open and note odor.

"Chemical" test.—Set up a steam distillation apparatus. Put 50 grams of the suspected flour into a 500 ec. flask, add 100 cc. of 10% sulphuric acid⁵ and insert immediately into the steam distillation train. (This should be done without delay to avoid any possible loss of naphthalene by volatilization, as the flour generates some heat when mixed with sulphuric acid). Agitate to obtain a homogeneous mixture. Heat the flask with a boiling water bath and steam distill, generating the steam in an auxiliary flask, until the distillate measures about 125 cc., receiving the distillate in a pear-shaped separatory funnel. Shake the distillate with 5 cc. of chloroform, separate, and dry the chloroform layer with anhydrous calcium chloride. Drop a few small pieces of anhydrous aluminum chloride into a dry 6-inch pyrex test tube and heat until sublimed. Stopper, and allow to cool. Introduce the dried chloroform extract, stopper, and manipulate the tube to bring the chloroform into contact with the aluminum chloride sublimate. In the presence of naphthalene a violet color appears in a very short time.

Wholesome wheat flour when subjected to the test gave a very satisfactory blank test; there was no reaction whatever with the aluminum chloride, the chloroform remaining colorless.

Summary

A reliable method has been described for the detection of naphthalene in flour in concentrations as low as 1.5 to 1.0 parts of naphthalene per 100,000 parts of flour. This is for the method as described, i. e., using a 50-gram sample. In other words the method is capable of detecting 0.5 mg. of naphthalene. It is safe to assume, then, that naphthalene can be detected by this procedure in dilutions higher than 1 part in 100,000 by using a proportionately larger sample.

^{4 &}quot;Technology of Bread Making," Baker's Helper Company, Chicago, (1921), page 565.

5 The use of sulphuric acid is an important feature of this method. The acid hydrolyzes the flour, giving soluble products and thereby releasing adsorbed naphthalene. If water is used, as was the case in our earlier work, the flour starch gelatinizes, giving a very viscous, almost solid mass from which it is impossible to drive out the naphthalene.

BOOK REVIEW

Handbook for Bakers, by Albert F. Gerhard, Baking Department, William Hood Dunwoody Industrial Institute. 484 pages. Century Vocational Series. Published by the Century Publishing Company, New York. 1925.

The subject matter of the book is divided into six major parts having the following titles: Part 1, Raw Material; Part 2, Bake Shop Equipment; Part 3, Technology of Breadmaking; Part 4, Bake Shop Management; Part 5, Cake Ornamenting and Decorating; Part 6, Sweet Goods Manufacture and Recipes. An appendix contains a dictionary of the technical terms used in the text.

Under "raw material" the author discusses the various ingredients used by the baker. While the major portion is devoted to bread dough ingredients, the materials of the sweet-goods baker receive some attention. The discussions are semitechnical in character, embracing a statement of the average composition of the various materials, some considerations of their function in the dough batch, their source, and use.

Part two has four subdivisions dealing with (1) Floor Plans and Layouts for Bakeries, (2) Floors and Decorations, (3) Baker's Machinery and Equipment, and (4) Bake Ovens. The plans given are confined to small and medium sized shops. Suggested arrangements of equipment are depicted for the manufacture of both bread and sweet goods in the same establishment.

The section on machinery deals primarily with the function of the machines rather than their operation. It is the shortest section in the book, and in view of its importance it is regrettable that more space is not devoted to it. The illustrations of various types of equipment are limited in number. The value of this part would be enhanced by showing the co-ordination of various machines in There are several significant omissions. working units. merry-go-round or tray-type proofer, which is extensively used and has an important place in the bake shop, is not mentioned in this section, altho mention is made of it elsewhere. Among other equipment not included in the discussion may be mentioned the sack cleaner, homogenizer, and steam generating systems for oven and proof box. The use of steam in baking is nowhere mentioned in the book. This constitutes an important omission. In the reviewer's opinion this is the weakest section of the book.

Part 3, on the technology of breadmaking, describes the various methods of manufacture in detail. Then follows a discussion of fermentation, enzymes, bread judging, and other technical con-